
Chapter 1

Clinker Burning: Material Technological Aspects

Clinker Burning - Material Technological Aspects

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1. INTRODUCTION

In the production of Portland cement a mixture of natural minerals is transformed into an intimate mixture of synthetic minerals having the required hydraulic properties.

$$\text{Natural minerals} \xrightarrow[\text{time (t), pressure (p)}]{\text{Temperature (T)}} \text{Synthetic hydraulic minerals}$$

This process is similar to that occurring during the transformation of sedimentary and igneous into metamorphic rocks, but with the exception that the time (t) is much shorter and that the pressure (p) is only 1 bar. Consequently, a high temperature is required.

During the transformation into clinker, two principal steps may be differentiated, namely the disintegration of the original rock structures followed by the formation of new ones. Even these categories can be subdivided as follows:

Disintegration of original structure

- mechanical crushing and grinding
- thermal decomposition
- structural rearrangement on heating (e.g. polymorphism)
- melting

Formation of new structures

- occurrence of intermediate products
- genesis and growth of final clinker minerals
- crystallization of liquid phase

1.1 Important Features

Several important features characterize the clinker formation process. These are:

- the clinker burning system is complex and occurs via a series of diverse mechanisms
- the transformation requires mechanical, thermal and electrical energy
- the reaction rate is slow in comparison with homogenous reactions (i.e. gas or liquid phase reactions). This leads to the necessity of high temperatures, extended reaction times, and finely dispersed materials
- the desired hydraulically active clinker minerals are not all stable at normal temperature, and so the hot clinker must be rapidly cooled
- the quality of the product is determined by the
 - ⇒ clinker chemistry
 - ⇒ clinker microstructure

1.2 Control of the burning process

The transition into clinker is influenced by both material and process technological aspects, namely:

- ◆ Material technological aspects
 - raw meal burning behavior including burnability, dust formation, coating behavior, granulation of clinker, etc.
 - The quantity and properties of the liquid phase
- ◆ Process technological aspects
 - temperature profile
 - kiln atmosphere
 - fuel type
 - flame characteristics
 - etc.

1.3 Basic Aspects of the Material Changes Involved in Clinker Formation

To properly understand the material changes occurring, it is an advantage to have a good knowledge of the most basic characteristic aspects associated with clinker formation. They are listed in the following table:

Table 1 Important aspects of the understanding of chemical reactions

Aspect	Characteristic Features
Reaction Pathway	indicates the intermediate products occurring between reactants and products
Reaction Mechanism	type(s) and reaction(s) taking place
Reaction Kinetics	indicates rate at which the final products are produced
Reaction Thermodynamics	dictates whether reaction will at all be possible, and what the heat and temperature requirements will be

It is therefore logical, when considering the production of Portland cement clinker, that consideration should be given to these and earlier mentioned points. In the following pages, a review will be given of the principal material aspects associated with clinker formation.

2. REACTION PATHWAYS ENCOUNTERED DURING CLINKER FORMATION

2.1 General Considerations

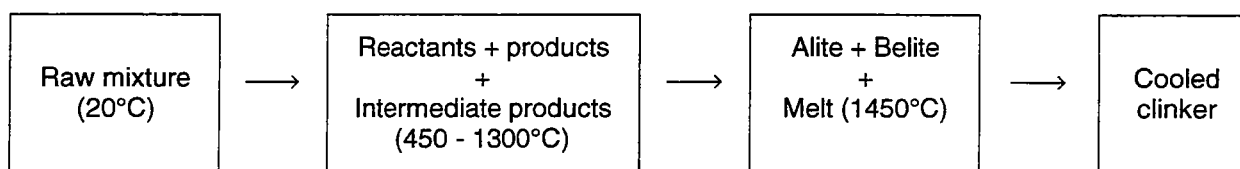
Cement clinker is an intermediate product in the manufacture of the hydraulic binding agent known as Portland cement. By means of a single thermal treatment, a mixture of the non-hydraulic, naturally occurring minerals calcite, quartz, clays and feldspars, it is transformed into the intimate mixture of hydraulically active minerals alite, belite, aluminate and ferrite, called Portland cement clinker. Like other products such as ceramics, refractories, bricks, etc., cement clinker can be considered as being synthetically produced rock. **The thermal treatment of heating and cooling, responsible for this “metamorphosis”, is termed “clinkering”** and, with the exception of a small number of shaft kilns, is carried out in one of the several types of rotary kilns. As has already been discussed, only a short specific range of mixtures of calcareous and siliceous minerals can be transformed into Portland cement clinker.

To fully describe the pathway of clinkering, it is necessary to consider the following aspects:

- ♦ the chemical and mineralogical content of the raw mix
- ♦ the overall sequence of reactions
- ♦ the chemical and mineralogical nature of the intermediate products

2.2 Basic Sequence of Reactions

During the heating and cooling of the clinker formation process, a complex series of reactions takes place within the rotary kiln, exhibiting a wide spectrum of reaction mechanisms. Concerning first the reactions involved, the following summarizes the general sequence of events taking place during the formation process.



As can be seen, the raw mixture is not transformed into the final cement clinker by rapid subjection to the required clinkering temperature. The process of clinker formation, as demanded by the construction of the rotary kiln, takes place over a wide range of temperatures, during which a complex mixture of reactants, intermediate and final products often coexist. Even after reaching the maximum temperature (approx. 1450 °C), a certain time must also elapse before a clinker of acceptable quality is produced.

In somewhat more detail, the principal sequence of events occurring and the temperature range over which they take place, can be represented as shown in Table 2:

Table 2 Sequence of reactions occurring in a rotary kiln

Temperature range (°C)	Type of reaction
<u>Heating:</u>	
20 - 100	Evaporation of H ₂ O
100 - 300	Loss of physically adsorbed water
400 - 900	Removal of structural H ₂ O (H ₂ O and OH groups) from clay minerals
>500	Structural changes in silicate minerals
600 - 900	Dissociation of carbonates
>800	Formation of belite, intermediate products, aluminate and ferrite
>1250°	Formation of liquid phase (aluminate and ferrite melt)
approx. 1450	Completion of reaction and recrystallization of alite and belite
<u>Cooling</u>	
1300 - 1240	Crystallization of liquid phase into mainly aluminate and ferrite

From Table 2, several points can be observed, namely:

- that the dissociation of carbonate minerals does not take place at any single temperature but occurs over a temperature range (600 - 900 °C)
- that, with respect to the formation of clinker minerals, three important stages can be distinguished:
- formation of belite, aluminate and ferrite over a wide temperature range starting at approx. 800 °C
- start of appearance of liquid phase and commencement of formation of principal clinker phases (alite) at approx. 1250 °C
- that the aluminate and ferrite found in the final clinker are formed by crystallization of the liquid phase during the cooling cycle. The individual aluminate and ferrite crystals formed during the heating cycle at >800 °C lose their identity by melting (> 1260 °C) to form the liquid phase

2.3 Mineralogical and Chemical Characteristics of Raw Mixes

During a detailed study performed by the Materials Division of the raw meals and slurries from all the plants of the "Holderbank" Group, a mineralogical and chemical analysis of a large number of mixes was undertaken. The following Tables 3 and 4 list the large variety of observed minerals and the range of raw mix chemistry.

Table 3 Minerals frequently found in cement raw mixes

Type	Example
Carbonates	calcite CaCO_3 , aragonite CaCO_3 , dolomite $\text{CaCO}_3 \cdot \text{MgCO}_3$, ankerite $\text{CaCO}_3 \cdot (\text{Mg, Fe}) \text{CO}_3$, magnesite MgCO_3 , siderite FeCO_3
Simple Oxides	quartz SiO_2 , cristobalite SiO_2 , hematite Fe_2O_3 , magnetite Fe_3O_4
Feldspars	potassium feldspars $(\text{Na, K}) \text{Si}_3\text{O}_8$ and plagioclase series $(\text{Na, Ca}) (\text{Si, Al}) \text{Al}_2\text{Si}_2\text{O}_8$
Sheet silicates*	minerals of the mica and chlorite groups (e.g. biotite, muscovite, chlorite), clay minerals (e.g. kaolinite, montmorillonite, illite, palygorskite) and other sheet silicates (e.g. pyrophyllite) *
Hydroxides*	Al-hydroxides (e.g. boehmite), Fe-hydroxides (e.g. goethite, limonite)
Sulfides and sulfates	pyrites FeS_2 , anhydrite CaSO_4 , gypsum $\text{Ca SO}_4 \cdot 2\text{H}_2\text{O}$
Fluorides	fluorspar CaF_2

*see chapter 4 for chemical formulae

Table 4 **Range of chemical compositions (dry basis) from which OPC clinker is normally produced**

	Parameter	\bar{x}	x min.	x max.
Chemistry (wt %)	L.o.I.	35.5	33.8	37.3
	SiO ₂	14.4	12.8	16.0
	Al ₂ O ₃	3.2	2.4	4.6
	Fe ₂ O ₃	1.8	1.0	3.8
	CaO	42.4	39.0	44.2
	MgO	1.3	.6	4.0
	SO ₃	.37	.08	1.1
	K ₂ O	.60	.08	1.4
	Na ₂ O	.17	.04	.58
	TiO ₂	.17	.10	.34
	Mn ₂ O ₃	.12	.07	.82
	P ₂ O ₅	.11	.04	.50
	Cl	.03	.01	.19
Ratios	SR	2.9	1.8	3.9
	AR	1.9	0.7	3.2
	LSF	94.0	85.4	103.4
Bogue Mineralogy	C ₃ S	59	39	84
	C ₂ S	19	0	41
	C ₃ A	8	7	13
	C ₄ AF	9	5	19

From the preceding data it is evident that the various mixes are composed of very different minerals and in addition vary within a certain range in their chemical composition. In spite of these differences, Portland cement clinkers composed of the same hydraulically active minerals are produced from all these mixes. The fact that such a diversity of mixes results in the same end product, underlines the complexity of the transformation process.

2.4 Intermediate Products

The clinkering reaction does not take place in a single direct step from the natural to the final minerals, but proceeds via intermediate products. These intermediate products can be observed by heating up raw mixes in the laboratory or by withdrawing samples from various points along the kiln. This latter method, although more difficult to carry out, has the advantage over the laboratory method in that those intermediate minerals, whose presence is also dependent on the kiln gas atmosphere, are observed. The following table lists the most commonly encountered intermediate minerals.

Table 5 Intermediate minerals encountered during clinker production

Type	Mineral Name	Chemical Composition
Simple Sulfates	anhydrite	CaSO_4
	arcanite	K_2SO_4
Compound Sulfates	"sulfate"-spurrite	$2(\text{C}_2\text{S}) \cdot \text{CaSO}_4$
	"calcium"-langbeinite	$\text{K}_2\text{Ca}_2(\text{SO}_4)_3$
Compound Carbonates	spurrite	$2(\text{C}_2\text{S}) \cdot \text{CaCO}_3$
Simple Chlorides	sylvite	KCl
Calcium Aluminates	mayenite	$12 \text{CaO} \cdot 7 \text{Al}_2\text{O}_3$
		$\text{CaO} \cdot \text{Al}_2\text{O}_3$
Calcium Ferrites		$2 \text{CaO} \cdot \text{Fe}_2\text{O}_3$
Calcium Alumino-Silicates	gehlenite	$2 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$

That these materials are formed at all, when it is considered that the final equilibrium products are alite, belite, aluminate, and ferrite, can be explained as follows:

Table 6 Reasons for the formation of the intermediate products

<ul style="list-style-type: none"> the intermediate products are preferentially formed by kinetically faster reaction rates the intermediate products are the reaction products of localized zones in the meal charge, i.e. local equilibrium but not overall equilibrium was reached (for example gehlenite formation) the intermediate products are really the equilibrium products at the given temperature and gas atmosphere, but not at the final clinkering temperature (the formation of spurrite is a typical example)
--

The most important intermediate product, however, is not a crystalline product at all, but is the liquid phase first formed above ca. 1250 °C, and which only forms crystalline products (mainly aluminate and ferrite) after cooling.

2.5 Liquid Phase

The composition of the raw mix determines

<ul style="list-style-type: none"> temperature at which liquid will first be formed amount of liquid formed at any given temperature the physical properties of the liquid at any particular temperature, especially its viscosity

2.5.1 Temperature of Liquid Formation

The following are the lowest melting temperatures of various mixtures pertinent to Portland cement production:

Components	Temperature °C of liquid formation
C - S	2065
C - S - A	1458
C - S - A - F	1338
C - S - A - F - M	1300
C - S - A - F - M - N	1280

Due to the inclusion of additional oxides (e.g. K_2O , TiO_2 , Mn_2O_3 , etc.) the lowest formation temperature of the liquid phase in clinker is in reality around 1250°C.

2.5.2 Quantity of Liquid

Although most raw mixes show about the same minimum temperature of liquid formation, the quantity of liquid formed at this and progressively higher temperatures varies according to the raw mix chemistry.

In the Portland cement relevant parts of the system C - S - A - F, in which melting begins at 1338 °C, the composition of the liquid is:

CaO	-	55 %	
SiO ₂	-	6 %	Alumina ratio
Al ₂ O ₃	-	22 %	(AR) = 1.38
Fe ₂ O ₃	-	16 %	

The percentage liquid forming at various temperature (1338, 1400, and 1450 °C) is given in Table 7.

Table 7 Formulae used for estimating the quantity of the liquid phase according to Lea & Parker

Temperature °C	Quantity of liquid phase
1338	AR > 1.38: $6.1 Fe_2O_3 + MgO + Na_2O + K_2O$ AR < 1.38: $8.5 Al_2O_3 - 5.22 Fe_2O_3 + MgO + Na_2O + K_2O$
1400	$2.95 Al_2O_3 + 2.2 Fe_2O_3 + MgO + Na_2O + K_2O$
1450	$3.0 Al_2O_3 + 2.25 Fe_2O_3 + MgO + Na_2O + K_2O$

Because MgO has limited solubility in the liquid, there is a restriction of 2 % maximum MgO which can be incorporated into these equations.

For the majority of clinkers, the quantity of liquid formed at 1450 °C varies according to the above formula from approx. 20 to 30 %. Figure 1 shows the quantity of liquid formed at the given temperature for several Group plant clinker, the influence of MgO and alkalis being included.

Figure 1 Quantitative change of liquid phase with temperature
(INFLUENCE OF MgO, Na₂O AND K₂O INCLUDED)

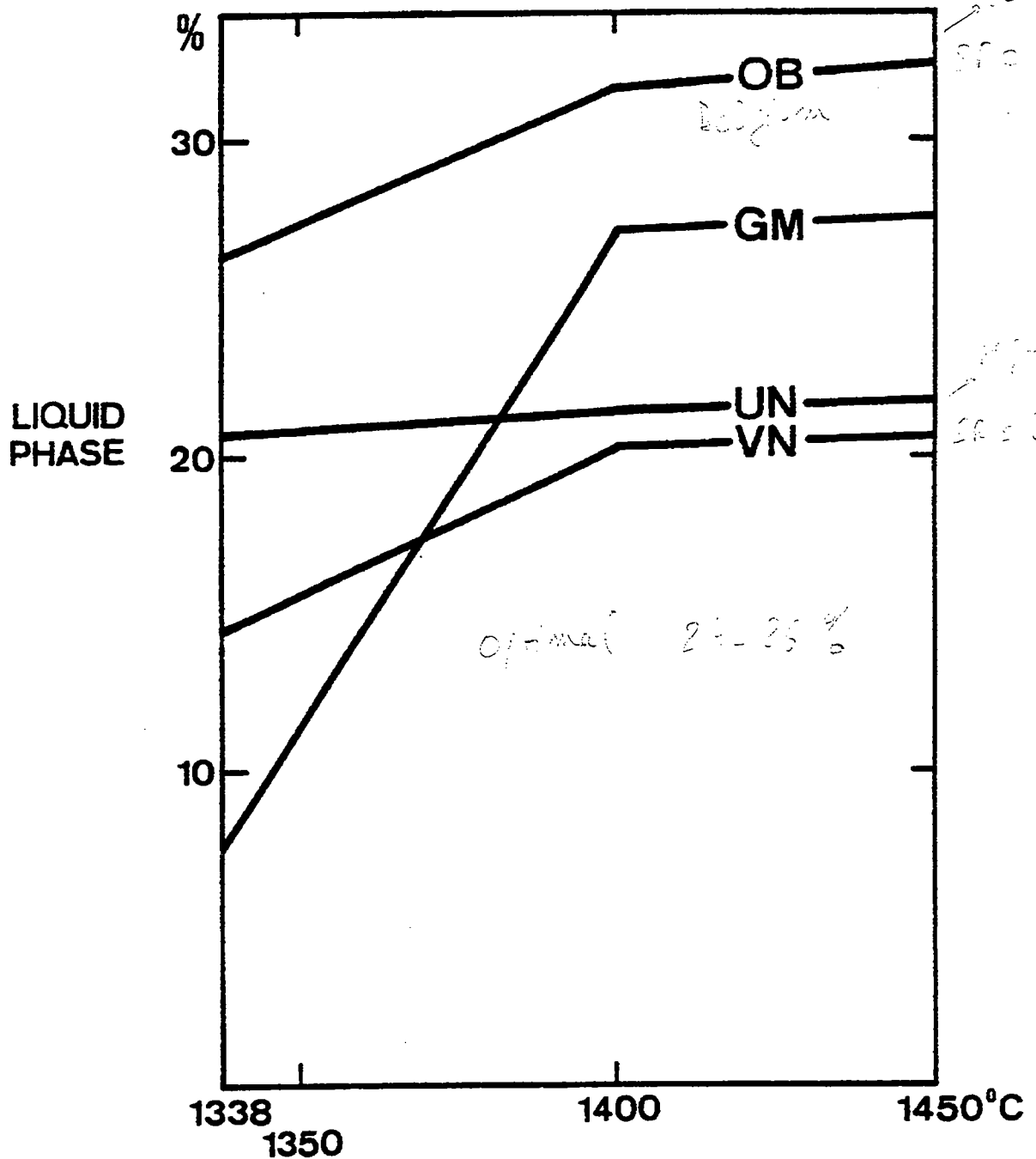
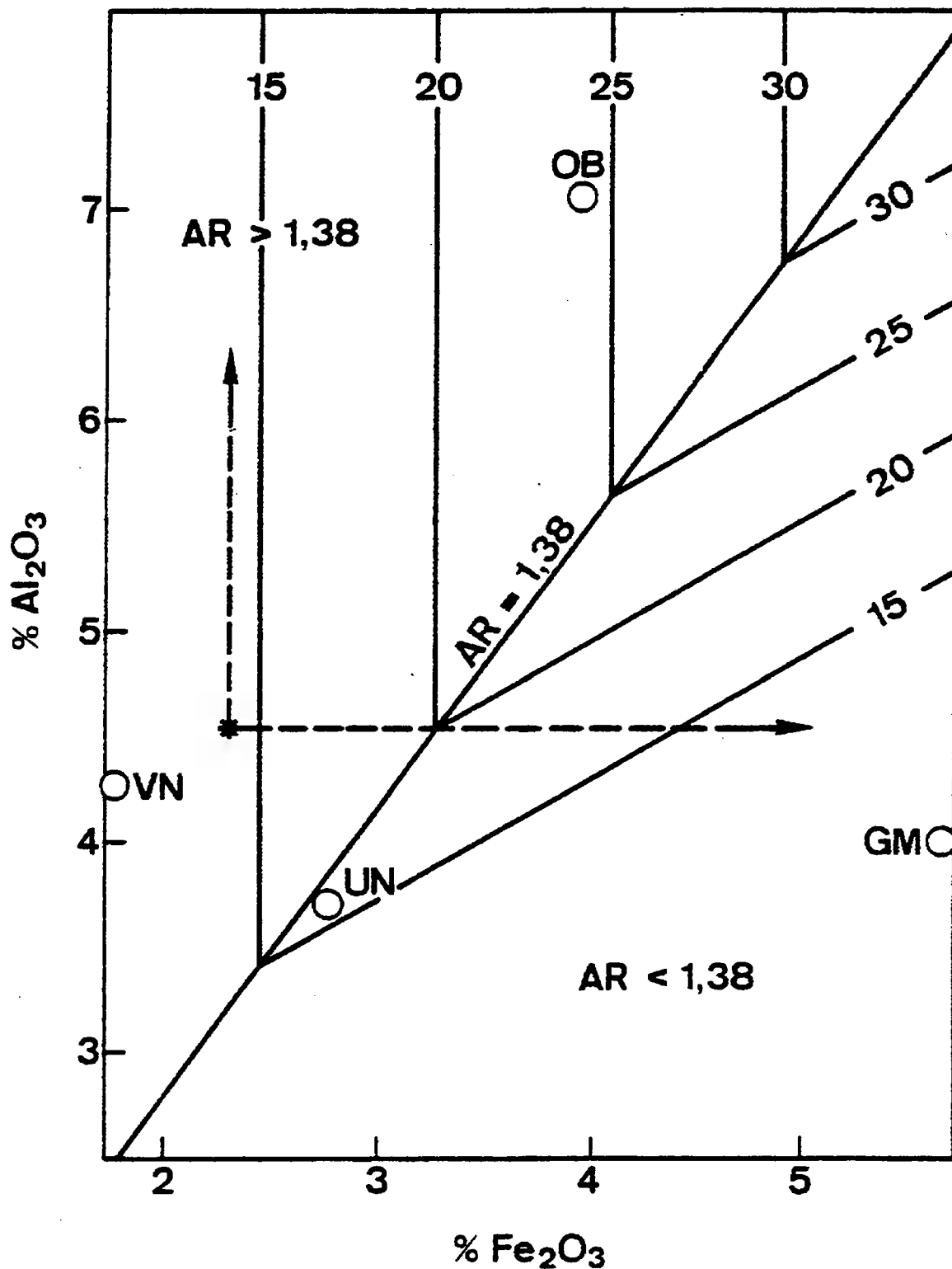


Figure 2 displays graphically the influence of Al₂O₃ and Fe₂O₃ alone on the quantity of liquid formed at 1338 °C, the solid contours representing the percentage of liquid formed. It can be seen that the effect of adding Fe₂O₃ or Al₂O₃ on the proportion of liquid formed at 1338 °C is influenced strongly by the alumina ratio. If in a clinker composition containing 4.5 % Al₂O₃ and 2 % Fe₂O₃, for example, the Fe₂O₃ content is held constant and the Al₂O₃ content is increased, the percentage of liquid remains unchanged at 14 %, because the iso-Fe₂O₃ contour lies parallel to the iso-liquid contour in this region. If, however, the iron content is increased and the Al₂O₃ content remains constant, the proportion of liquid at first increases rapidly until at 3.3 % Fe₂O₃ it attains a maximum of 21 %. With further increase in Fe₂O₃ the

quantity of liquid decreases. Therefore, the most effective use of Al_2O_3 and Fe_2O_3 - with respect to liquid formation at 1338 °C - occurs when the two are used in the weight ratio of 1.38.

Figure 2 Quantity of liquid phase at 1338 °C



AR = Alumina ratio

OB, GM, UN, VN = Different Plants

At 1400 °C and above increasing Al_2O_3 and / or Fe_2O_3 always result in a larger quantity of liquid phase, Al_2O_3 being the one with the larger influence.

2.5.3 Viscosity of Liquid Phase

The viscosity of the liquid phase diminishes exponentially with increasing temperature and at 1400 °C is reduced by addition of fluxing components in the following order:



With increasing SiO_2 content of the melt and to a lesser extent with increasing Al_2O_3 , appreciable increases in viscosity occur.

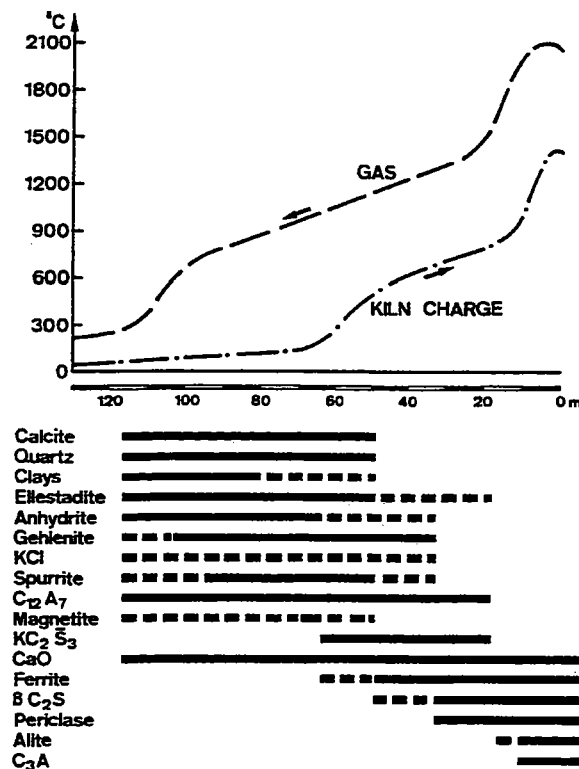
2.6 The Overall Reaction Sequence

Several different approaches have been used in the past to display the sequence of events taking place during the formation of cement clinker. These differ mainly in the aspect chosen, the following examples giving emphasis to differing features.

2.6.1 Display Based on Qualitative Change of Minerals from Samples taken from an Operational Kiln

The minerals existing at various points during the production process in the kiln can be seen in Figure 3. It is worth noting that the feed contains several minerals (e.g. KCl, spurrite, $C_{12}A_7$, CaO) that were not present in the freshly milled raw mix. This is due to the return of dust to the slurry feed.

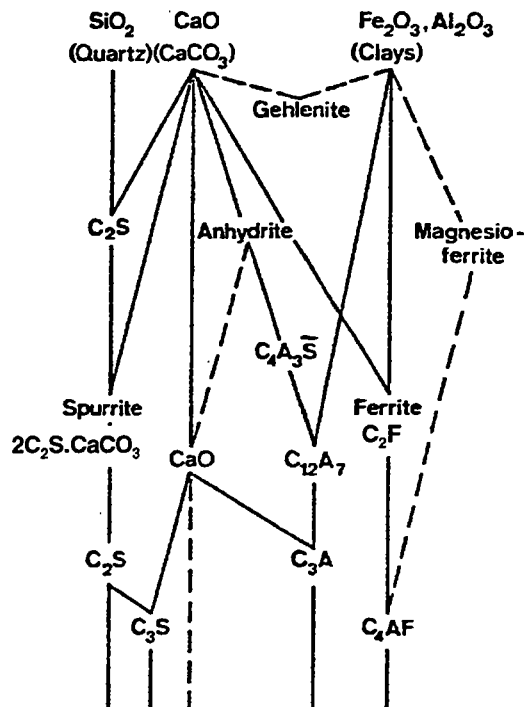
Figure 3 Minerals identified at different locations (long wet kiln)



2.6.2 Schematic Display according to Chemistry

A recent example of this approach to clinker formation is proposed in Figure 4.

Figure 4 Sequence of compound formation according to chemical composition

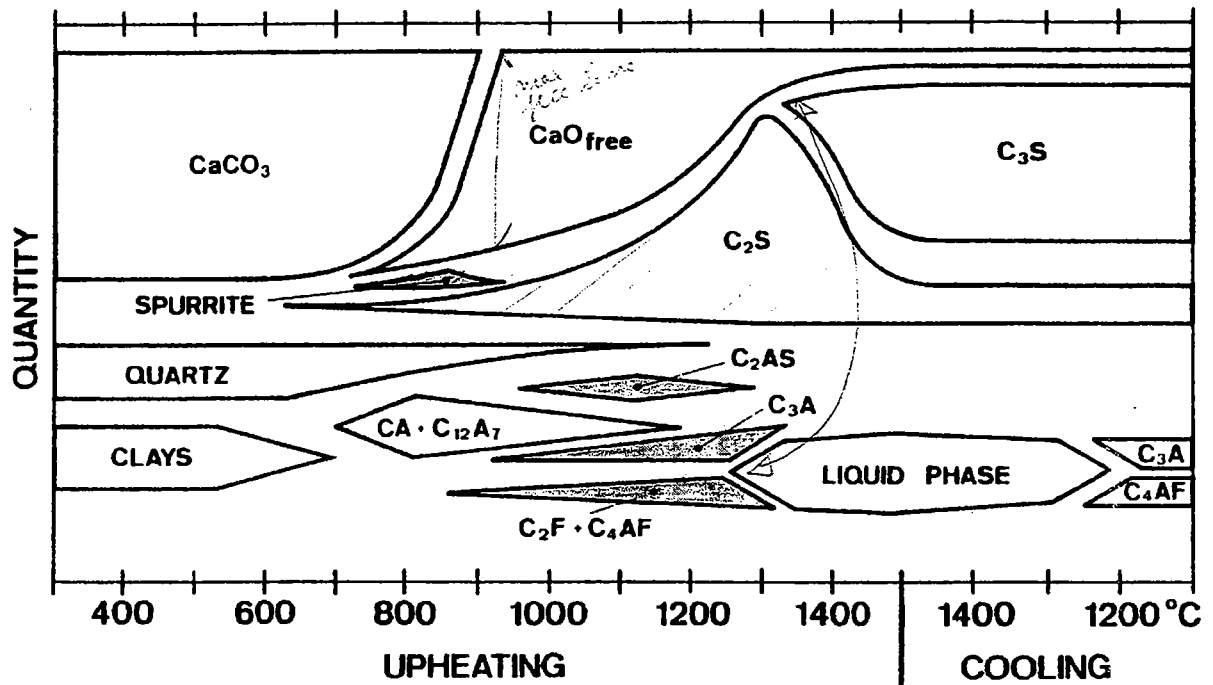


In order to allow an overall picture to be quickly gained, it must be mentioned that the SiO_2 content of the clay minerals and the pressure of feldspars have been omitted. Of interest in the above display is that the presence of spurrite is considered as being a normal intermediate product and not only a component found solely in kiln deposits.

2.6.3 Quasi-Quantitative Display of Minerals Present at Various Temperatures

An informative schematic display based mainly on laboratory studies depicts in a quasi-quantitative manner changes of the various minerals with temperature. This is shown in Figure 5

Figure 5 Quasi-quantitative variation of minerals with temperature



3. REACTION MECHANISMS

3.1 Definitions

For the discussion of reaction mechanisms the following concepts with regard to states of matter and types of reaction will be employed.

3.1.1 States of Matter

All matter can be assigned at any specific temperature to at least one of the three defined states of matter, namely to the solid, liquid, or gaseous state. Each of these states has specific properties which allow a simple distinction between them to be made as follows:

State of Matter	Properties
solid	definitive volume and definite shape
liquid	definitive volume, assumes shape of container
gaseous	neither definitive volume nor definite shape

Under specific conditions (of temperature and pressure) it is possible for more than one state to coexist with another. An example demonstrating this effect is, of course, water which at various temperatures and pressures can coexist in the liquid/gas, solid/liquid and solid/liquid/gas states.

3.1.2 Classification of Reactions

Chemical reactions may be classified according to their type, namely:

Type	Example from clinker burning
structural change	high quartz \leftrightarrow low quartz
decomposition	$\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2$
combination	$2\text{CaO} + \text{SiO}_2 \leftrightarrow \text{C}_2\text{S}$

A further differentiation of these reaction types may be made:

- ♦ According to the state of matter

reaction type	Example from clinker burning
solid - solid	quartz and free CaO \rightarrow belite
solid - liquid	liquid phase \rightarrow crystallization of aluminates + ferrite
solid - gas	$\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2$
liquid - liquid	-
liquid - gas	drying process, volatilization of alkalis, etc.
gas - gas	$\text{CO} + 1/2 \text{O}_2 \leftrightarrow \text{CO}_2$

- ♦ according to rate controlling step (kinetics of reaction)

Type	Example from clinker burning
diffusion	formation of alite
phase boundary	quartz + free CaO \rightarrow belite (initial reaction)
nucleation	liquid phase \rightarrow crystallization of aluminates + ferrite alite formation

For many reactions the rate controlling pressure may not be known.

Since clinker burning is a most complex chemical process, it is not surprising that most of the mentioned reaction types are operative during the process. In the following, examples of these reaction types taking place in the kiln during production will be considered.

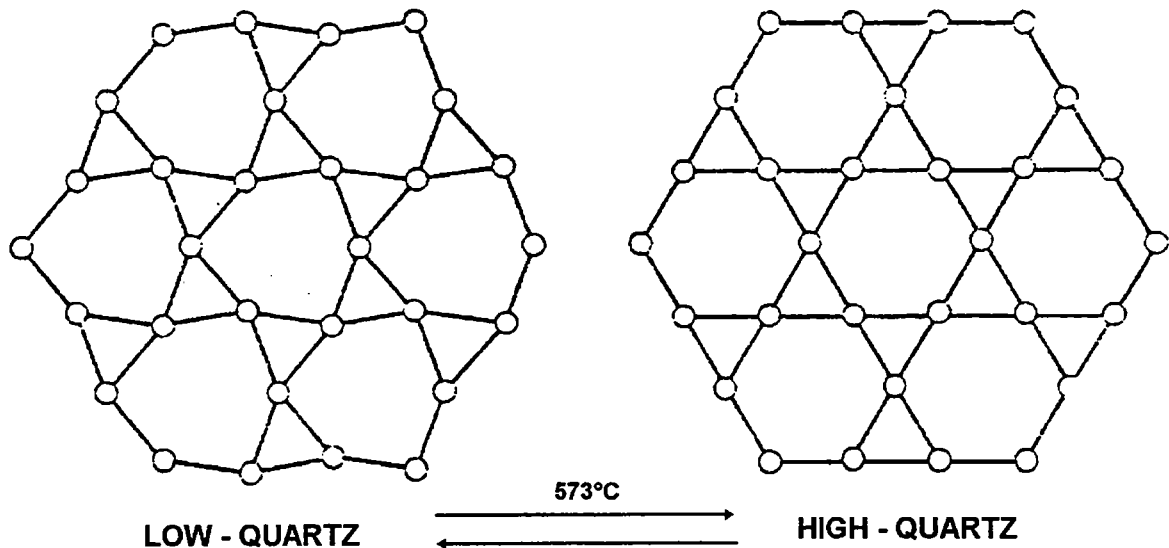
3.2 Examples

3.2.1 Structural Changes

This type of change occurring within single minerals in the solid state is also called a polymorphic transition (see paper 4). In this process the chemical composition of the minerals remains constant, but the spatial arrangement of the component atoms alters, usually upon reaching a specific temperature. Relevant examples of such polymorphic transition in clinker burning include the following:

- a) The low - high quartz inversion (both have composition SiO_2)

Figure 6 Arrangement of the atoms in low and high quartz

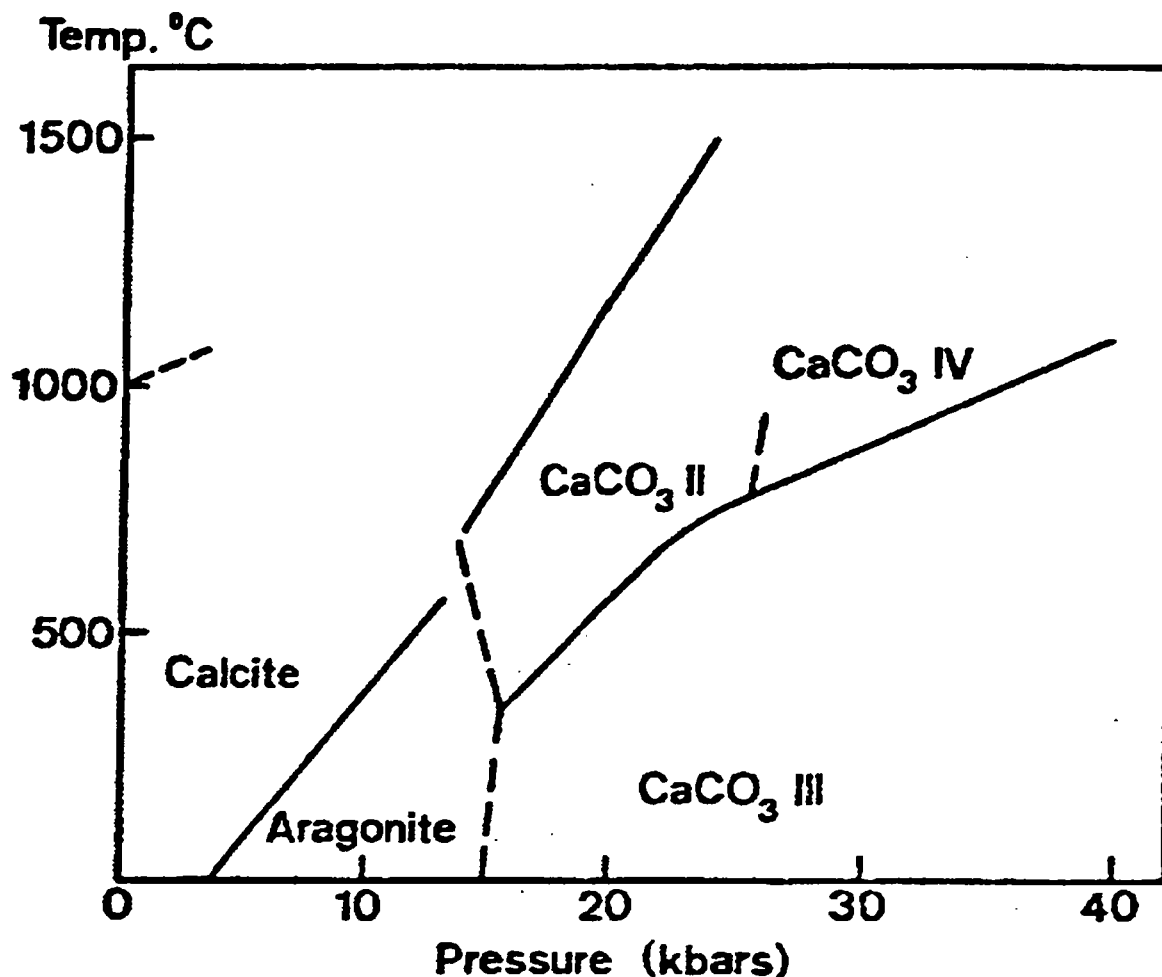


In this transition the distorted low form, stable under 573 °C, changes into the more ordered high modification, the stable species above the transition temperature.

- b) aragonite → calcite inversion (both have composition CaCO_3)

Aragonite present in the raw meal transforms on heating into calcite. Consequently, kiln dust always contains calcite and not aragonite. The reason for this transition is, that under normal atmospheric pressure calcite and not aragonite is the stable form of CaCO_3 . This can be easily seen in Figure 7, showing the stability conditions of calcite and aragonite.

Figure 7 Stability conditions of the various forms of CaCO_3



c) alite and belite transformations

Even more important than the polymorphic transitions in the raw materials are the structural changes occurring in the principal clinker minerals alite and belite. These occur during both formation and cooling of the clinker, and contribute to the complexity of the clinker system. These transitions will be discussed in more detail in paper 13, pages 11 - 13.

3.2.2 Decomposition Reactions

The principal decomposition reactions encountered during clinker production include the following:

solid / gas type

- ◆ dehydroxylation of the clay minerals (kaolinite, etc.)
- ◆ decarbonation of the carbonate minerals (magnesite, dolomite, calcite, spurrite)

solid / solid type

- ◆ decomposition of alite

Characteristic of this reaction type is that the single reactant is transformed into two products.

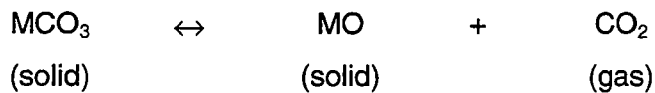
a) Dehydroxylation of the clay minerals

The removal of structural water from the clay minerals is a complex decomposition, as it further involves structural changes of the dehydrated product. This may be demonstrated for one of the simplest of the clay minerals compounds kaolinite, $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$.

There are two alternative theories about the changes that kaolinite undergoes when it loses water at about 500 - 600 °C. One theory is that the anhydrous aluminosilicate $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ is formed, the other than an intimate mixture of amorphous silica and alumina results

b) Decarbonation of the simple carbonate minerals

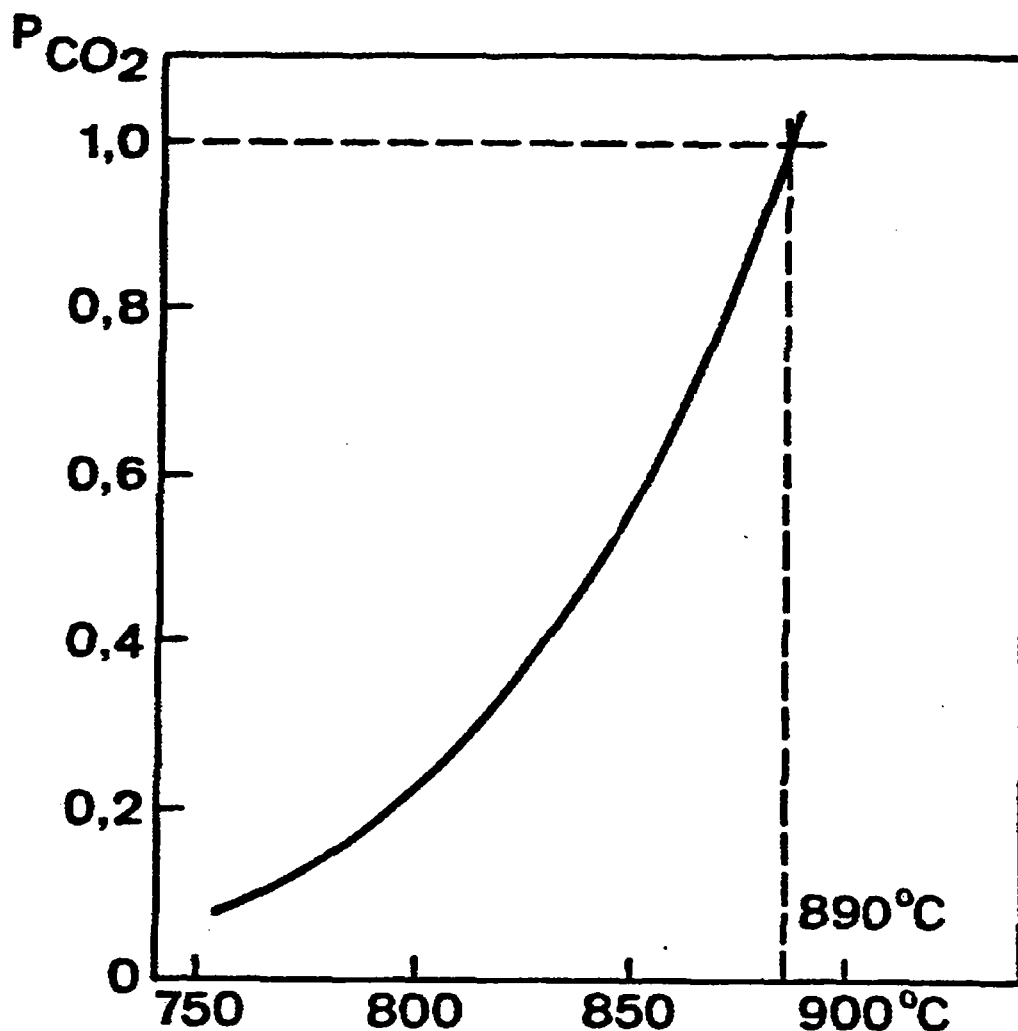
These reactions are of the type



where M
 = Ca (Calcite)
 = Ca/Mg (Dolomite)
 = Mg (Magnesite)

in which, if the CO_2 is not removed, there exists an equilibrium between the reactant and the reaction products. At any single temperature, both the degree of decarbonisation of the carbonate and the partial pressure of CO_2 (i.e. $p\text{CO}_2$) are fixed, providing equilibrium has been achieved. With increasing temperature the $p\text{CO}_2$ value increases until a certain given temperature the value equals atmosphere pressure as shown in Figure 8, so that the carbonate will completely decompose.

Figure 8 **Equilibrium dissociation pressure of calcite with temperature**



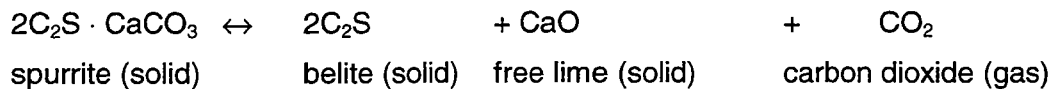
Under conditions in which the CO_2 is constantly removed (e.g. in a flowing gas atmosphere at reduced pressure in which the $p\text{CO}_2$ value is lower than the equilibrium level) decomposition of the carbonate will take place at a reduced temperature.

In the simple carbonates found in cement raw mixes, the temperature at which the equilibrium $p\text{CO}_2$ level attains 1 bar is as follows:

Mineral	Temp (°C)	$p\text{CO}_2 = 1 \text{ bar}$
Calcite	890	
Dolomite	745 and 890	
Magnesite	650	

c) Decomposition of compound carbonates (e.g. spurrite)

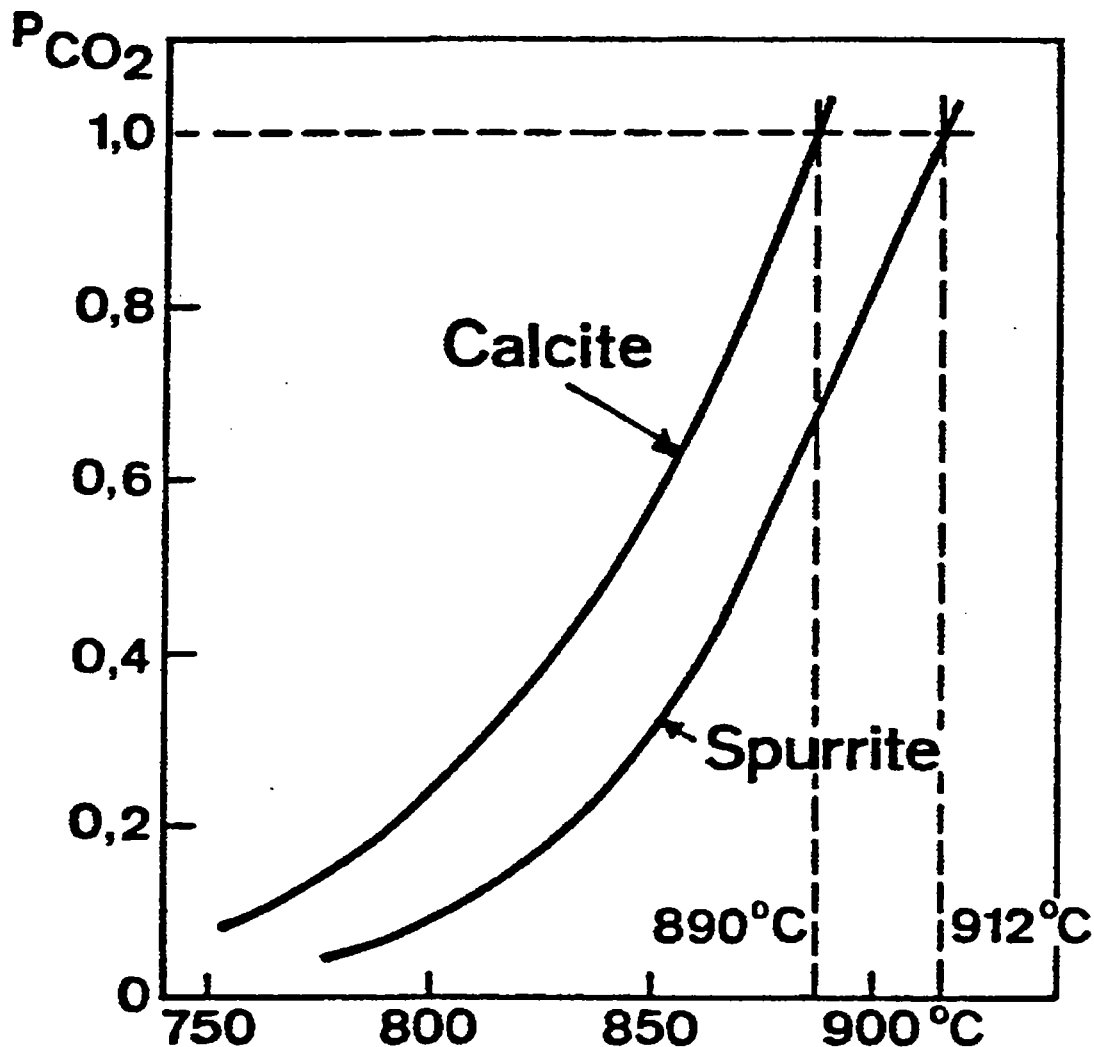
The decarbonisation of spurrite $2\text{C}_2\text{S} \cdot \text{CaCO}_3$ proceeds according to the equation



Just like the simple carbonates, the above equilibrium is reversible, and its extent depends on the temperature and $p\text{CO}_2$ value. Unlike the simple carbonates, two solid reaction products are formed, belite and free CaO, which at the temperature associated with spurrite decomposition under normal pressure, cannot react with each other.

The equilibrium $p\text{CO}_2$ value for spurrite is given in Figure 9 along with that pertaining to CaCO_3 .

Figure 9 Equilibrium dissociation pressure of calcite and spurrite with temperature



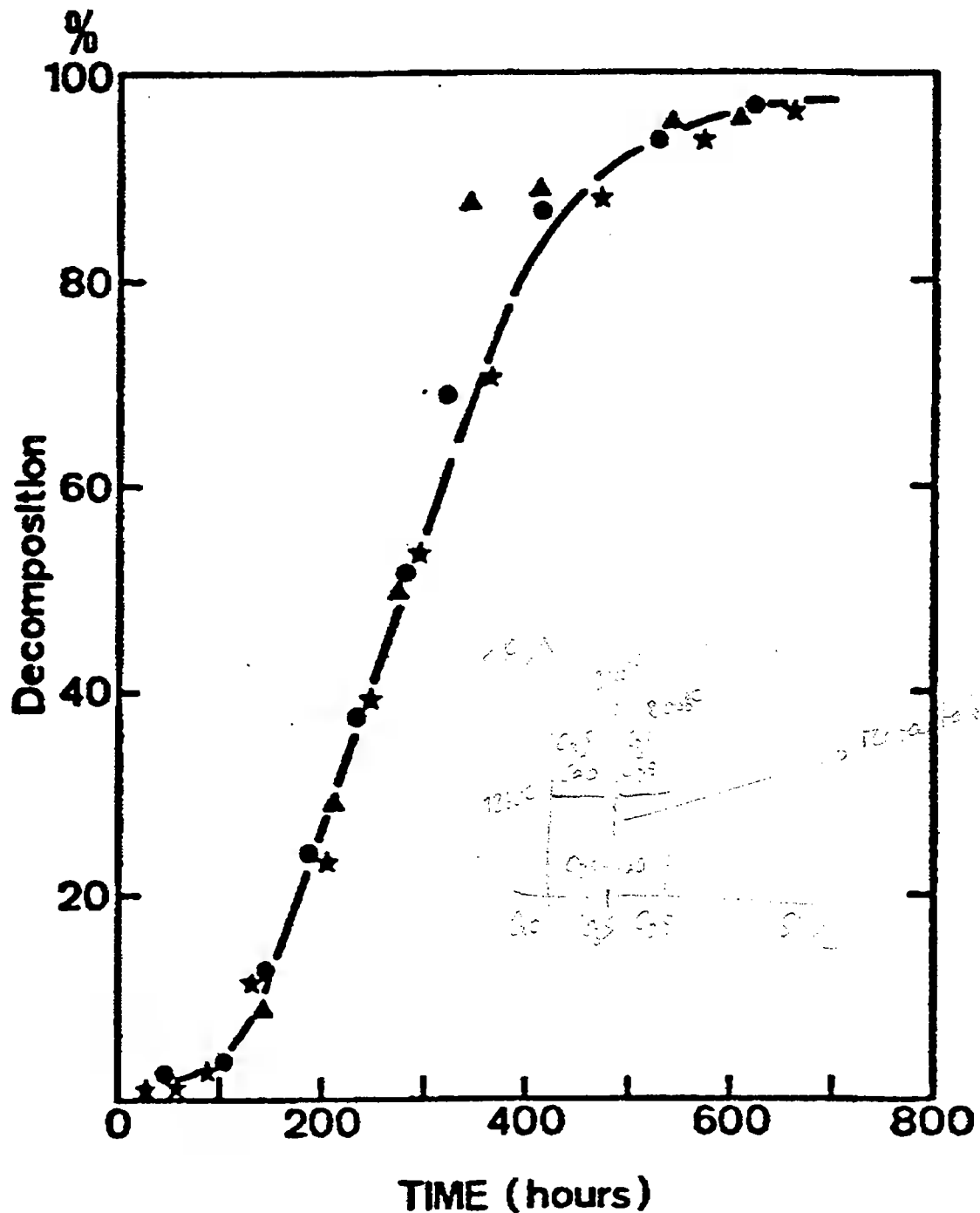
From the figure it is evident that **spurrite is thermally more stable than calcite**. As a consequence of the greater stability of spurrite, it may form in cement kilns either by direct reaction of calcium carbonate and silica, or by reaction of CaO, Ca_2SiO_4 and gaseous CO_2 .

The formation of spurrite with the latter mechanism may occur only in a small range of temperatures above the $CaCO_3$ decomposition temperature, for example, between 890 °C and 912 °C at 1 bar CO_2 pressure.

d) Decomposition of alite

A reaction of the solid-solid decomposition type which can, under certain circumstances, occur during clinker cooling, is the decomposition of alite. From the phase diagram for the system $CaO - SiO_2$ it can be deduced that C_3S has a lower limit of stability at 1250 °C, below which it will decompose into two solids, C_2S and CaO . The maximum rate of decomposition occurs at 1175 °C, at which temperature the S-shape decomposition curve (Figure 10) indicates that the initial decomposition is controller by nucleation of the products on the C_3S surface.

Figure 10 Decomposition of C_3S at 1175 °C



As can be deduced from figure 10, the rate of decomposition is so slow that for the cooling rates encountered during clinker cooling, the decomposition of C_3S should not be observed.

In the case of impure C_3S , i.e. clinker alite, the rate of decomposition is appreciably accelerated by:

- the presence of lime and C_2S nuclei
- the presence of Fe^{2+} , H_2O and $K_2SO_4 / CaSO_4$ melts

This aspect will be further considered in paper 13.

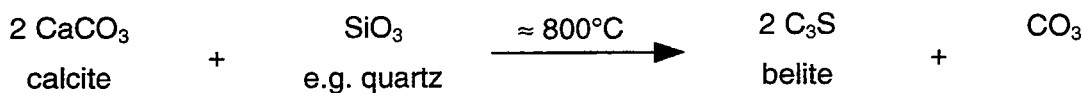
3.2.3 Combination Reactions

The main combination reactions are the formation of the two major phases, the calcium silicates alite and belite, the only principal phases remaining unmelted at the highest clinkering temperature. The other major phases, aluminates and ferrite, although formed by combination reactions during heating, are melted at the highest temperatures and are present in the final cooled clinker as crystallization products of the melt.

a) Belite formation

The formation of belite starts at $\approx 800^\circ\text{C}$ and is mainly formed by solid-state reaction. In many raw mixes it is formed in quantities exceeding those found in the final clinker (see Figure 5) and then further reacts with free lime (via the liquid phase) to yield alite, the quantity of belite thus falling back to that finally observed.

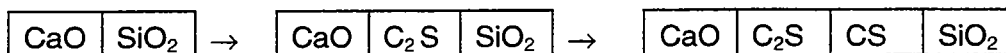
Belite formation (see Figure 4) is the result of a combination between the calcite and silica components of the raw mix.



Although the $p\text{CO}_2$ value of calcite does not reach 1 bar until 890°C , the initial formation of belite does take place at lower temperatures, due to the stability of the C_2S phase.

During the solid state reaction of silica and calcite (or CaO) the first reaction product is always C_2S . This can be seen in Figure 11.

Figure 11 Sequence of appearance of phases in the solid state reaction of CaO and SiO_2



showing the order of appearance of phases at a $\text{CaO} / \text{SiO}_2$ interface. Only later does the most silica rich phase CS appear as a result of reactions between C_2S and SiO_2 . This demonstrates the remarkably strong nature of the belite formation reaction. At temperatures at which solid state reactions occur, the formation of C_3S does not take place due to its thermal instability.

The rate limiting mechanism by which belite is formed (after an initial phase boundary controlled reaction) depends on the diffusion of ions through the solid state. The rate of this reaction is thus dependent on:

- the path distance that the diffusing species have to travel
- defects in the reactant's crystal lattices.

The former factor is dependent on both the size of the CaO and SiO_2 particles, and the effective contact area between them. It is this easy to understand why finely milled and/or densely intergrown powder mixtures react faster than large-grained coarse ones, and thus, why cement raw meals must be finely ground and intimately mixed.

From the results of many studies, the main diffusion species is known to be the Ca^{2+} ion which migrates into the solid SiO_2 , although evidence does exist to indicate that the diffusion of Si^{4+} into CaO can occur to a lesser extent.

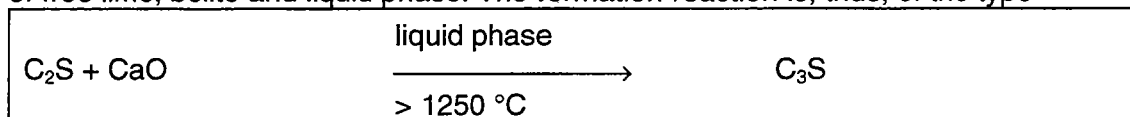
That the Ca^{2+} ion is the major diffusing species is confirmed by the well known fact in clinker formation that the quartz must be finer ground than the limestone if complete reaction is to take place.

b) Formation of alite

The formation of alite commences only when the temperature is above its lower stability limit of $\approx 1250^\circ\text{C}$. At that temperature, the liquid phase is also starting to form. Consequently the formation of alite is a liquid - solid reaction, as reaction via a liquid medium is faster than by solid state processes. In the laboratory, C_3S can be formed by the solid state reaction of CaO and SiO_2 , but this requires many hours at temperatures above those encountered during clinker formation. The resulting finely crystalline product must be rapidly quenched, at much faster rate than can be achieved in a production kiln, to prevent its decomposition at normal temperatures.

In the industrial production of clinker, the formation of alite and its stabilization is thus wholly dependent on the presence of the liquid phase.

At the temperature at which alite formation begins ($\approx 1250^\circ\text{C}$), the material consists mainly of free lime, belite and liquid phase. The formation reaction is, thus, of the type



From the results of many laboratory experiments, the rate controlling step is considered to be the movement (diffusion) of dissolved CaO through the melt. This is supported by the following observations:

- ◆ alite particles often contain belite inclusions (see paper 13)
- ◆ when free lime is added to an already formed clinker, and the mixture again heated, pores are to be found where the lime particles had been, surrounded by a zone containing only alite.

Again, as in the case of belite formation, the rate of reaction is influenced by

- ◆ the distance the CaO has to travel (depending on raw mix fineness and homogeneity), and in addition to the quantity and viscosity of the liquid phase (controls the gas with which the movement of CaO can occur).

quantity: 20 - 30 %

As the viscosity of the raw mix is reduced by



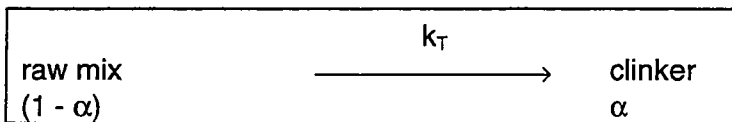
it can thus be appreciated that the presence of Fe_2O_3 and MgO in the liquid phase assists in the alite formation process.

4. KINETICS OF CLINKER BURNING

4.1 General Aspects

The burning of cement consists of a series of reactions taking place between finely divided solids, and it is only at temperatures above 1250°C that a liquid is formed and becomes the medium through which reaction occurs. When liquids or solutions react together, the actions usually occur rapidly and the products depend only on the composition of the reaction mixture and the temperature. With reactions between solids the conditions are very different. Reaction takes place at the surface of grains, and diffusion of fresh solid to the surface proceeds but slowly. If a particle of clay is imagined surrounded by particles of lime, the reaction will commence at the surface of the clay particle. This in turn will react with further clay inside. If complete combination is not attained, the stage to which the reaction has progressed depends not only on the temperature, but also on the time, or rate of heating and the general physical and chemical condition of the reacting materials.

This phenomenon of the rate of reaction can be schematically represented as follows:



where k_T is the **rate of reaction** at temperature T and α the extent of clinker formation after a certain time. The rate of reaction k_T is dependent on temperature and material characteristics (mainly mineralogy and fineness as expressed in the **fundamental Arrhenius equation**

$$k_T = Ae^{-E_a/RT}$$

- k_T = rate constant at temperature T
 T = reaction temperature
 R = gas constant
 E_a = activation energy
 A = frequency factor

From the above equation it can be seen that the rate of reaction

- increases with them T and contact surface between raw mix components (frequency factor A)
- decreases with higher activation energy E_a for raw mix components.

This can be illustrated as follows. Experience demonstrates that a raw mix composed of non-reactive minerals (high activation energy E_a) such as quartz, forms clinker more slowly than a raw mix incorporating more reactive components such as clay minerals or amorphous silica. The lower activation energy required for the reaction with lime results in a high rate of clinker formation. To compensate for the **slow reactivity** of the less reactive minerals, a **higher burning temperature and / or longer burning period** (longer clinkering zone) is required.

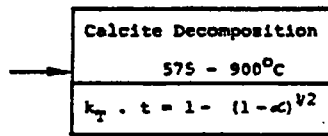
The quantitative characterization of the kinetics of clinker formation, however, is extremely complicated, due to:

- ◆ Portland cement having a range of chemical compositions and being produced from a wide spectrum of different minerals
- ◆ the transformation takes place via a series of sequential and simultaneous reaction steps of various types
- ◆ the burning process is not isothermal but occurs in a heating process
- ◆ the non-availability of a simple, precise method for determining the extent of reaction (α)

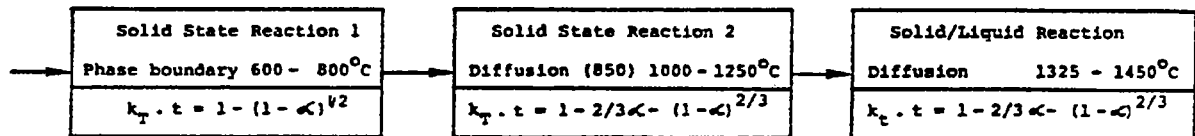
Various attempts have, in spite of the complexity of the system, been undertaken to evaluate the kinetics of clinker formation. An example is given in the following table.

Table 8 Various models for describing the kinetics of clinker formation

Parallel Decomposition Stage



Consecutive Reaction Stages



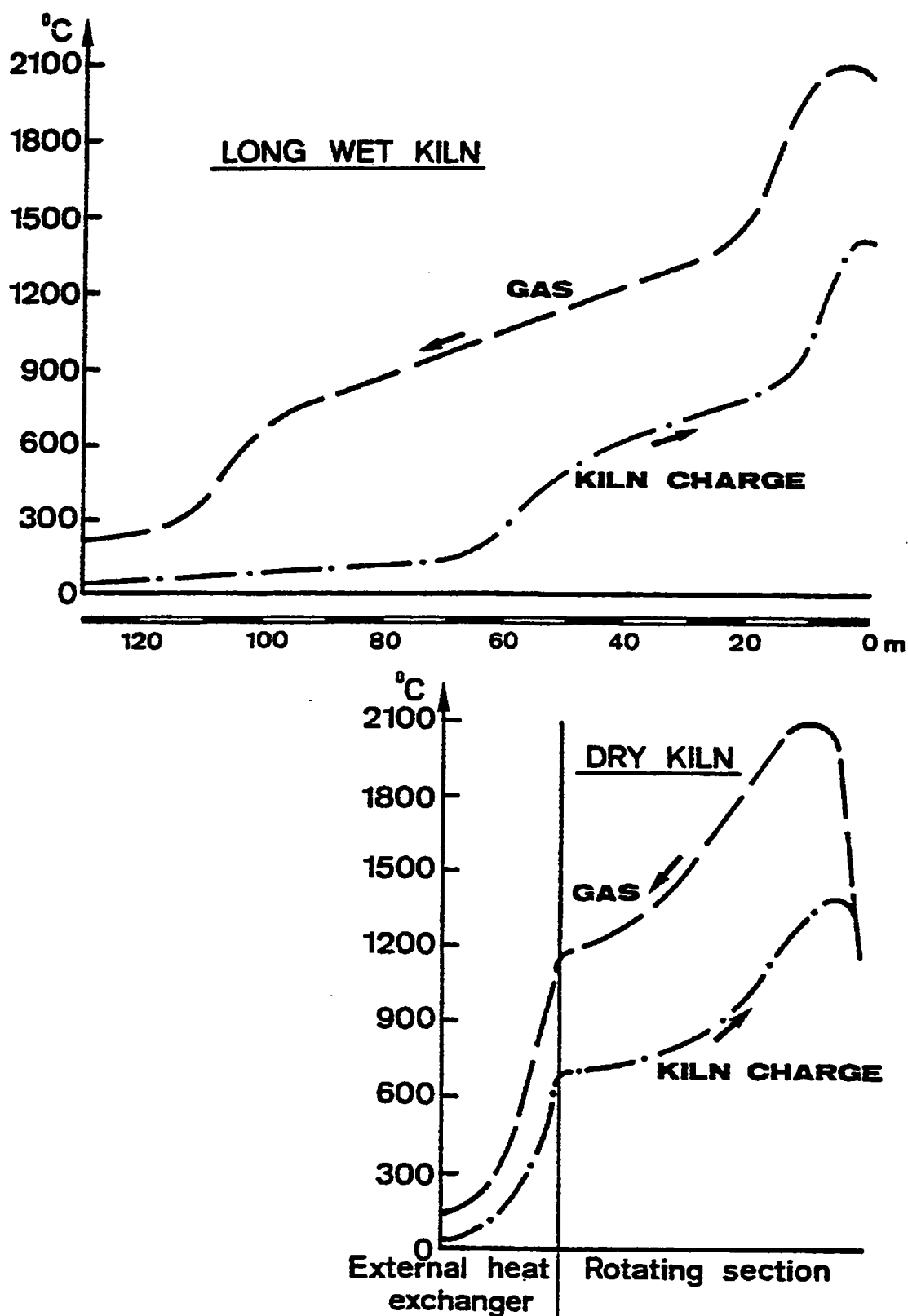
The main feature is that the process has been subdivided into four stages having different reaction mechanisms and rates.

For further details Report No. MA 75/2408/E may be consulted.

4.2 Practical Considerations

When comparing the overall reaction velocity with the kinetics of the individual stages (Table 8), it is known that the calcite decomposition, i.e. decarbonation of the raw meal, is not critical. **The combination reaction stages (solid/solid and solid/liquid) are the rate determining steps in the process.** The practical consequence of this is that it has been possible to replace the long rotary kiln by a suspension preheater kiln, in which the calcite decomposition may take place to a large extent within minutes. In the clinker formation stages, however, a rotary part of adequate length so as to allow sufficient reaction time, is indispensable. This is illustrated in Figure 12.

Figure 12 Temperature distribution in wet and dry process kilns



Consequently, to assess the progress of clinker formation, most consideration is given to events occurring after decarbonation.

In practice, the most convenient method of following the reaction is by measuring the rate of decrease of uncombined lime (i.e. free lime). This technique is illustrated in Figure 13 showing two raw mixes, I and II, of identical chemistry (LS = 95, SR = 3.2 and AR = 2.2) and similar fineness ($R_{200\mu} \approx 0.5\%$, $R_{90} \approx 7\%$ and $R_{60} \approx 15\%$). It is evident that the difference in mineralogy and actual particle size of the individual crystals influence both the mechanism and rate of reaction, especially at start of the clinker formation.

As can be seen in Phototable 1, mix I is composed of limestone and the fine-grained shale A which itself consists of finely mixed calcite (40 %) and siliceous (60 %) components, whilst mix II is composed of the same limestone but with the much coarser grained shale S containing a high proportion of coarse quartz particles. While raw mix I is considered to have a good burnability, raw mix II is considerably more difficult to burn.

Figure 13 Temperature change of DTA curves, phases identified and free lime

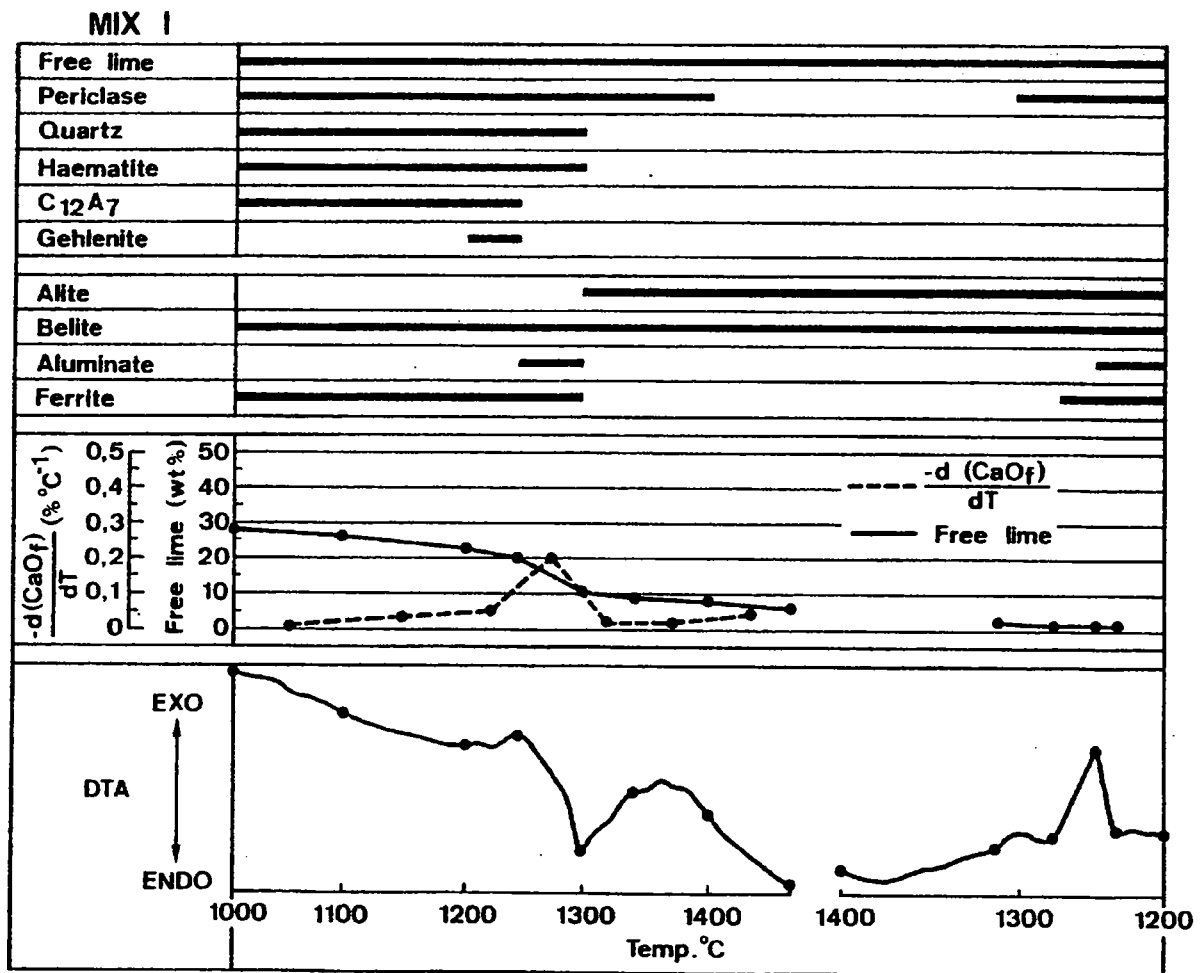
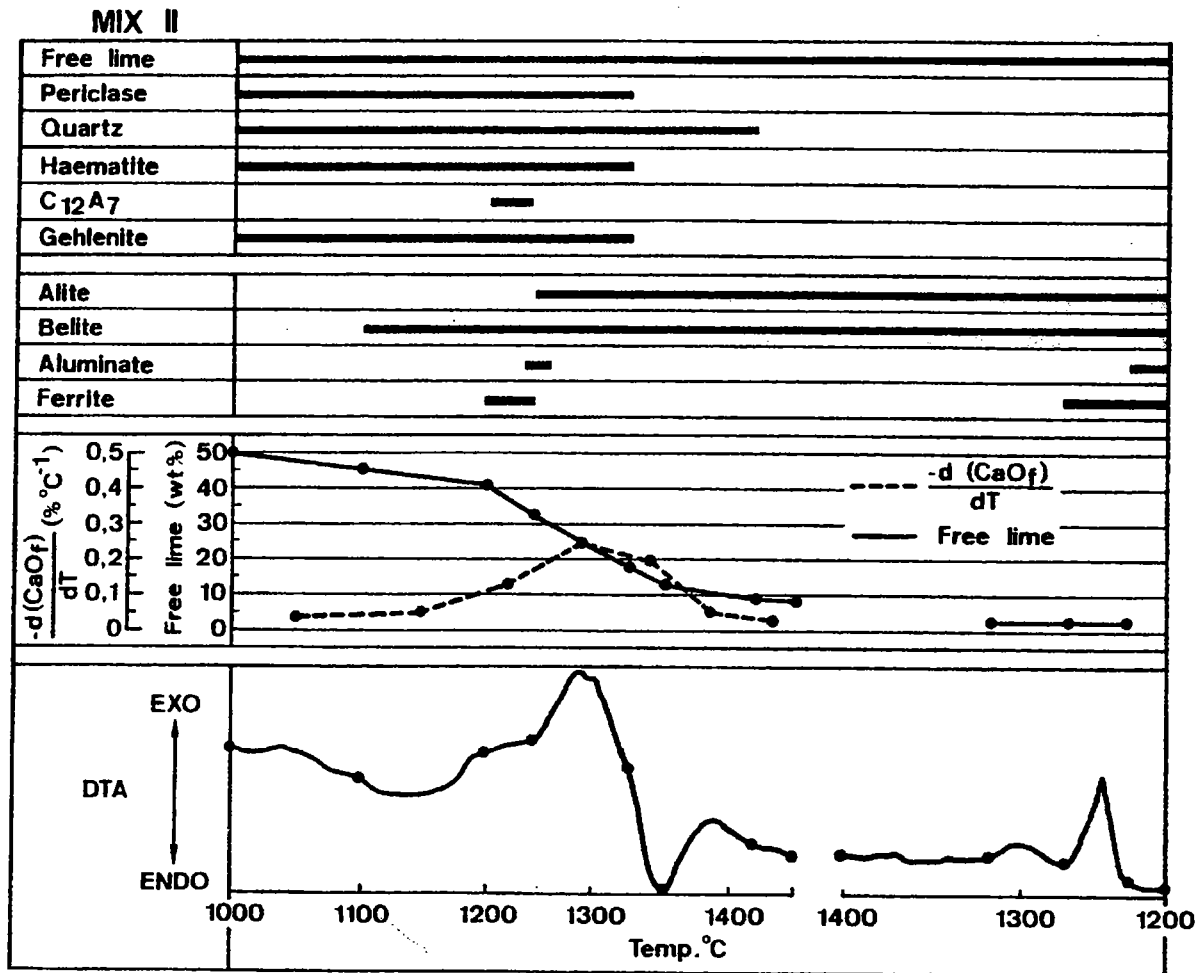


Figure 13 a Temperature change of DTA curves, phases identified and free lime

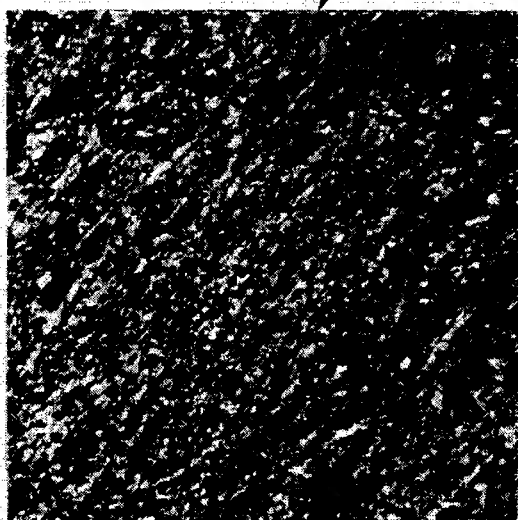


Phototable I Texture and Mineralogy of Mix Components

Limestone. 40 x

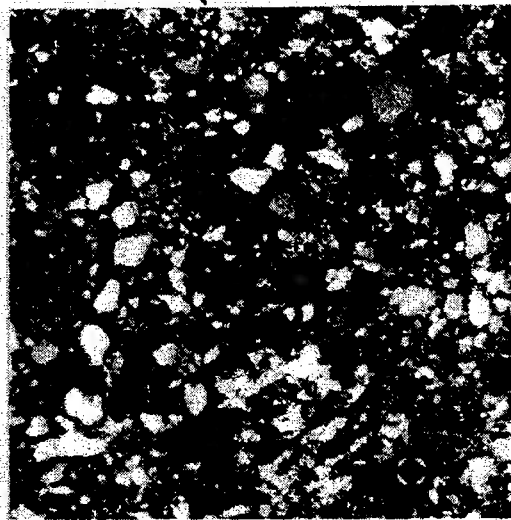


Raw Mix 1



Shale A. 40 x

Raw Mix 2



Shale S. 40 x

Designation	Limestone	Shale A	Shale S
Calcite	97 %	≈ 40 %	≈ 10 %
Dolomite	≈ 2 %	-	-
Quartz	traces	≈ 25 %	≈ 55 %
Chlorite	-	≈ 20 %	≈ 10 %
Illite and Micas	-	≈ 10 %	≈ 20 %
Pyrite	traces	≈ 2 %	traces
Feldspars	-	≈ 2 %	traces

4.3 Assessment of Raw Meal Burnability

From the foregoing it will be realized that a true determination of reaction kinetics is at best feasible in fundamental research. In practice, simple methods are mostly applied to assess the **"burnability" of a mix, i.e. the ease of formation of the clinker minerals**. Three distinct methods are practiced at the "Holderbank" Technical Center:

- ◆ "Holderbank" burnability test -
involves the heating of a raw mix under well defined laboratory conditions, and subsequent laboratory determination of the non-combined lime.
- ◆ Statistical burning model -
in which **ten material parameters**, proven to be of significance, influence the rate of clinker formation. The uncombined CaO value, of any raw mix, relative to that of a standard raw mix prepared from identical components, is calculated.
- ◆ Physicochemical burning model -
requires no standard raw mix. Only 4 parameters need to be considered.

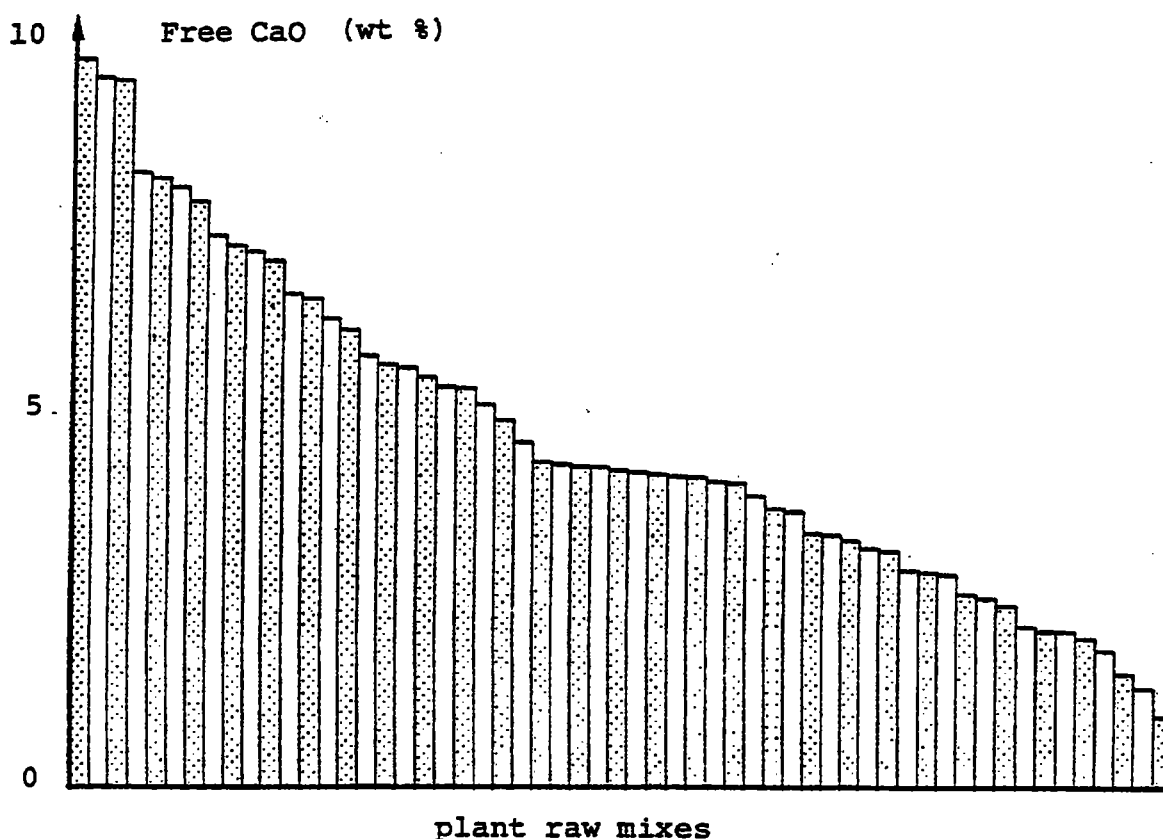
4.3.1 "Holderbank" Burnability Test

The "Holderbank" burnability test is based on the isothermal burning at 1400 °C of raw meal nodules, details of which can be obtained in paper 5, page 5/18 ff.

By being carried out under standard laboratory conditions, this test allows the determination of the **relative influence of the various material parameters to be ascertained, free from the influence of process technological disturbances**.

Typical results obtained by this test for the raw mixes of all Group plants are listed in Figure 14, arranged in order of decreasing free CaO, i.e. increasingly better burnability.

Figure 14 Range of CaO values determined by the "Holderbank" burnability test on plant raw mixes



The free lime value of the **laboratory** clinker extended from a minimum value of 0.94 % to a maximum value of 9.5 %. The values are distributed rather regularly around the mean value of 4.7 %. Based on this distribution and the corresponding plant experience, the burnability of raw mixes is ranked as follows:

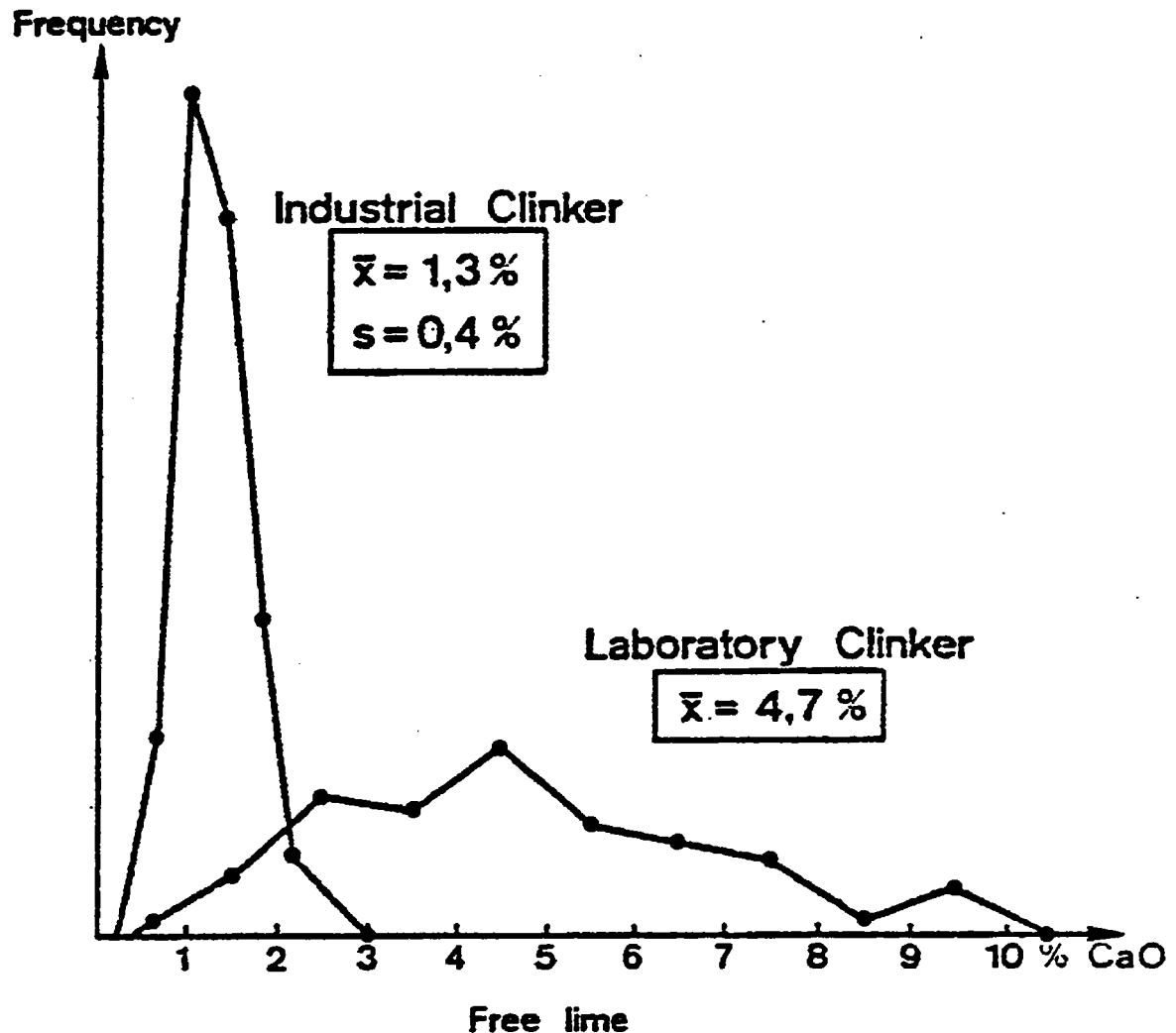
Evaluation	Free Lime %
very good	0 - 2
good	2 - 4
moderate	4 - 6
poor	6 - 8
very poor	> 8

This classification has been shown to be applicable over many years of practical experience.

With the same raw meals the free lime values of the industrial clinker vary within a much smaller range, from a minimum value of 0.6 % CaO_{free} to a maximum value of 2.8 % CaO_{free} . The mean free lime value of the clinker examined from the "Holderbank" Group is about 1.3 % CaO with a standard deviation of $s = 0.4$ %.

The difference between the distribution of free lime for the laboratory produced clinks of the burnability test and plant clinkers can be seen in Figure 15.

Figure 15 Distribution of free CaO values for plant clinkers and for clinkers produced by the "Holderbank" burnability test



This narrow range of free lime for plant clinkers can be explained by the quality requirements in the standards and of the market. The free lime values of industrial clinker, therefore, do not offer an explanation for the actual burning behavior of the raw mixes. The variability of raw mix laboratory burnability, as shown in Figure 14, is compensated by technological measures in the plant.

4.3.2 Statistical Burnability Model

In a quantitative evaluation of the data obtained by the "Holderbank" burnability test, a model has been developed - Statistical Burnability Model. The initial data for development of the model were the free lime values from burnability test at 1400 °C on 168 different raw mixes, the chemical and mineralogical composition, and the overall fineness of these mixes.

With this model, the 1350, 1400 and 1450 free lime values of other raw mixes from the same raw material components can be determined based on one single burnability test of one mix. In this way, the burnability model can be used as an instrument for **optimization of raw mixes** by allowing for the effect due to changes of the following factors:

<u>Chemical Parameters</u>	lime saturation, silica ratio, alumina ratio, K ₂ O + Na ₂ O, MgO
<u>Physical Parameters</u>	residue on 200 and 90 µm sieves, quantity of mica, quartz and iron minerals

An impression of the use of the statistical burnability model may be gained from the data listed in Table 9 and presented graphically in Figures 16 and 17. Using a standard raw mix (no. 2), of overall fineness $R_{90\mu} = 11\%$, and determined free lime value of 4.9 % that would be observed by varying the temperature, overall fineness and chemical composition have been **calculated**. For a series of mixes from any one set of components it is cheaper, quicker and equally accurate to use the model rather than burning each mix in the laboratory.

Table 9 Influence of fineness and chemistry on laboratory burnability of a raw mix

Mix No.	1	2 (Reference)	3	4	5	6	7
Chemical Characteristics							
LS		93,0		96,0	93,0	93,0	96,0
SR		2,37		2,37	2,60	2,37	2,60
AR		1,72		1,72	1,72	1,90	1,72
Fineness %R							
90 µm	8	11	17	11			
200 µm	0,2	0,4	0,6	0,4			
Free lime							
1350°C	5,6	6,3	7,1	7,5	7,1	6,2	8,4
1400°C	4,3	4,9	5,6	6,0	5,6	4,8	6,8
1450°C	3,0	3,5	4,1	4,4	4,1	3,5	5,1

Figure 16 Change of free lime with raw meal fineness

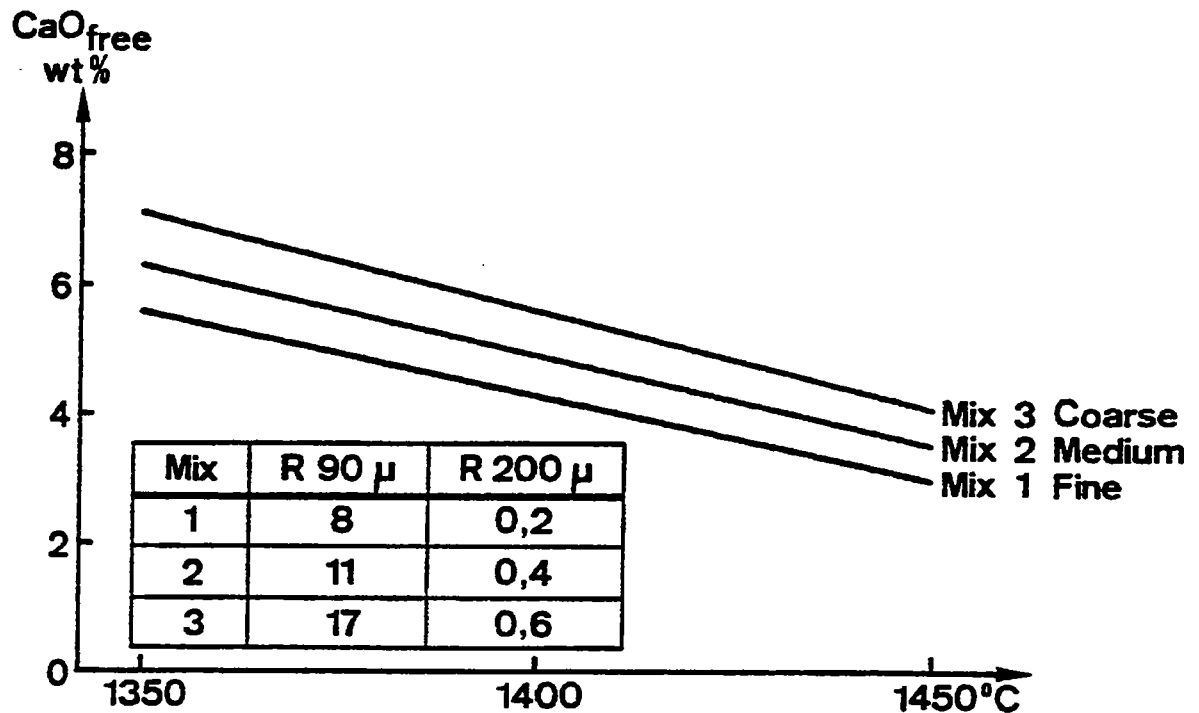
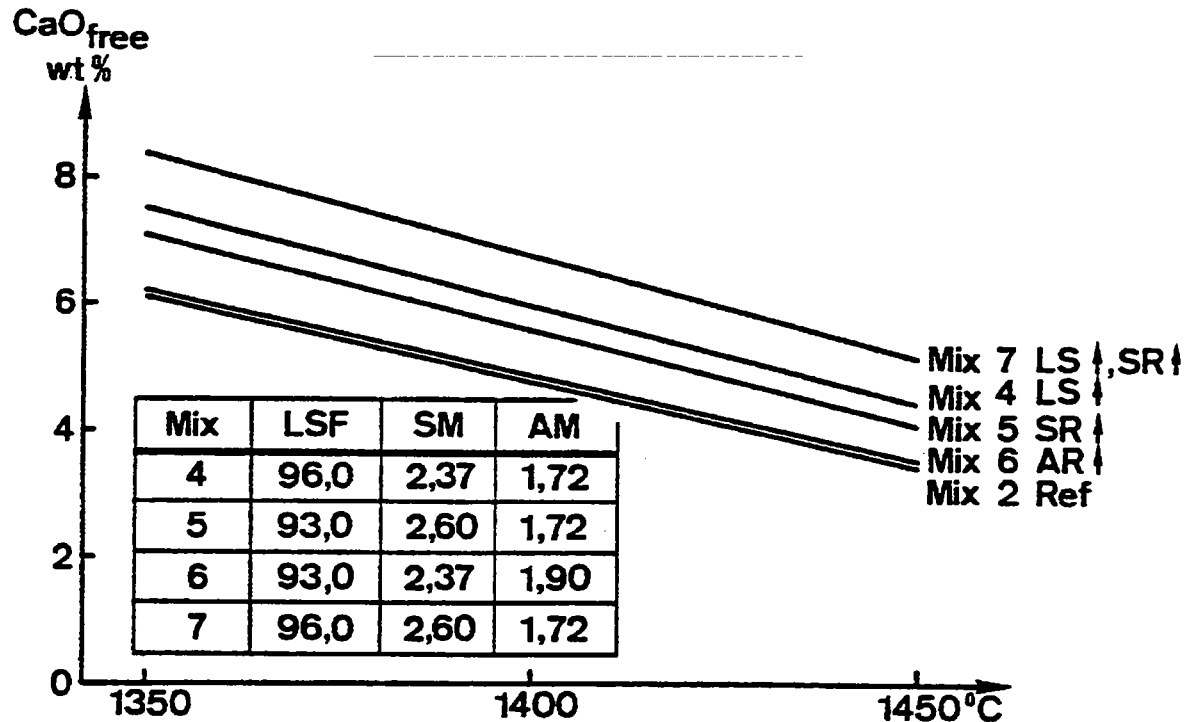


Figure 17 Change of free lime with raw meal composition



Influence of burning temperature

As can be seen in Table 9 and Figures 16 and 17, increasing the burning temperature results - as would be expected - in lower free lime values. Thus, for example, mix 2 (4.9 % free lime at 1400 °C) would contain 6.3 % at 1350 °C and 3.5 % at 1450 °C. The influence

of reducing the temperature 50 °C to 1350 °C is thus roughly the same as that resulting by increasing the lime saturation from 93 to 96%, as in mix 4.

Influence of raw meal fineness

Increasing the mix 2 residue on 90 μ from 11 to 17 %, results in the free lime at 1400 °C increasing to 5.6 %, while reducing the residue to 8 % decreases the free lime to 4.3 %. Increasing the residue to 17 %, thus has the same influence as that caused by raising the silica ratio from 2.37 to 2.6. Most practical use of being able to calculate the effects due to fineness is the assistance it gives when evaluating the optimum of raw meal mills.

Influence of LS, SR, and AR

The influence of increasing the LS, SR, and AR of mix 2 (LS 93, SR 2.7, and AR 1.72) can be seen in Figure 17. Increasing the AR to 1.9 has practically no effect, increasing the SR to 2.60 does, however, increase the free lime values (mix 5), but to a lesser extent than that caused by increasing the LS to 96. Increasing both the LS to 96 and the SR to 2.6, increases the free lime the most.

4.3.3 Physicochemical Burnability Model

Further investigations during recent years have contributed additional knowledge with regard to burnability. It has long been known that the amount of uncombined lime depends on:

- ◆ Specific reaction area, i.e. the area of contact between the grains
- ◆ local oversaturation, i.e. grain size of individual minerals
- ◆ ambient conditions, i.e. pressure, temperature, and burning time
- ◆ diffusion coefficient of CaO through the liquid phase, i.e. composition of the liquid phase
- ◆ amount of liquid phase formed during burning
- ◆ supply and demand of CaO

It has recently been found that all these influencing factors may be incorporated in four parameters, namely silica ratio, lime saturation, amount of oversized quartz grains and amount of oversized calcite grains. Pressure, temperature and burning time are considered to be constant.

Silica ratio (SR) and lime saturation (LS)

The formation of C_3S from C_2S and CaO is governed by the diffusion of CaO through the melt. The silica modules and lime saturation are sufficient to describe this chemical reaction quantitatively.

The amount of CaO which can be accommodated within the liquid phase and in which it can diffuse and thus react, is inversely proportional to the silica ratio. A linear relationship exists between max. lime saturation and silica ratio values at which no free lime can be observed.

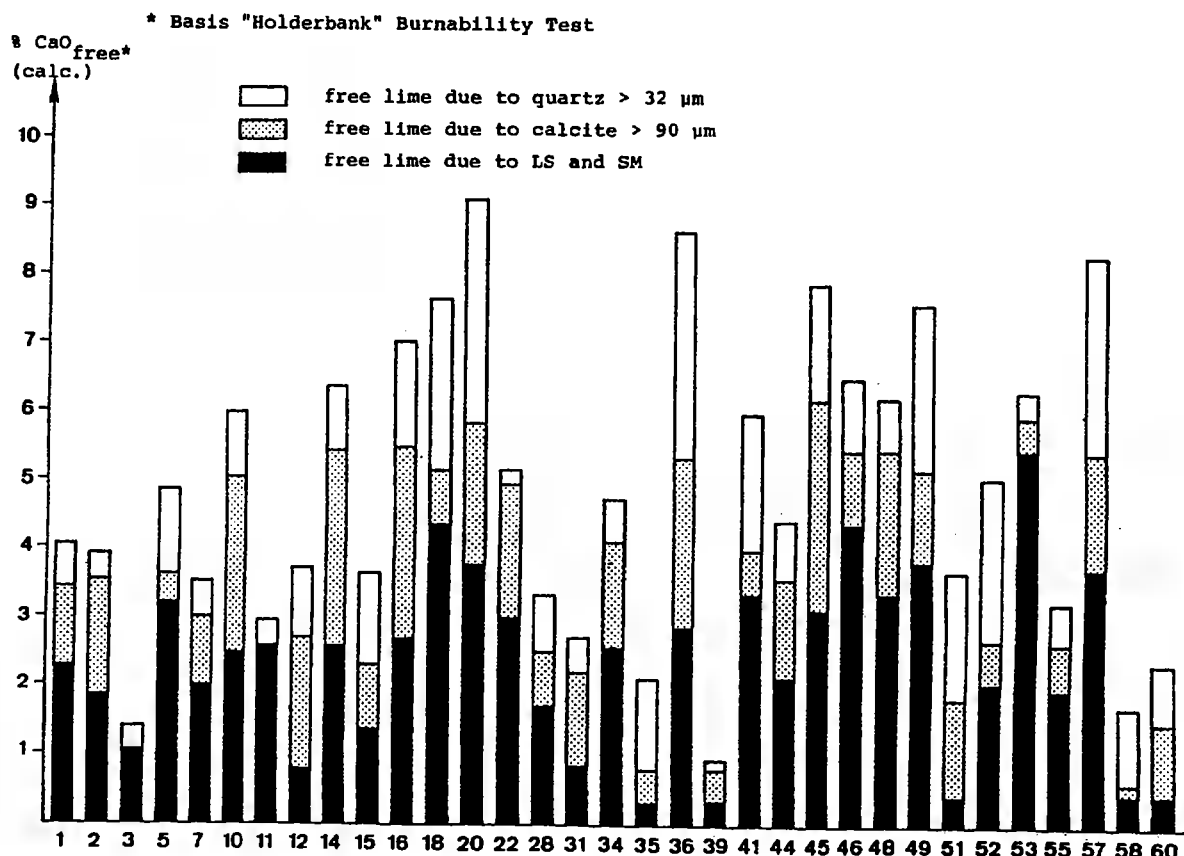
Quartz and calcite grains

Whether a grain of material reacts fully under given burning conditions depends on its diameter, structure and chemical composition. Monomineral particles above a certain critical size do not react fully, even after a long burning period. They are equivalent to local oversaturation of one chemical component. The overall raw mix residue is therefore not always a wholly reliable criterion for assessment of the burnability, unless the character of the grains is known. Quartz grains which exceed certain dimensions react with adjoining lime grains to form belite clusters. This prevents further reaction and gives rise to free lime.

Too large calcite grains result in CaO not being completely combined as also results from grains whose lime saturation is over 100 %.

For the "Holderbank" burnability test conditions the following grain diameters, quartz $\geq 32 \mu m$ and calcite $\geq 90 \mu m$, were found to be critical limits.

Figure 18 Influence of chemistry and coarse grains on burnability of raw mixes



An impression of the advantages offered by the physiochemical model may be drawn from the data presented in Figure 18 showing the influence of oversize quartz and calcite grains and of lime saturation (LS) and silica ratio (SR) on the uncombined CaO content of various industrial raw mixes.

The total free lime values calculated from the four mentioned parameters correlate well with the values determined experimentally by the "Holderbank" burnability test ($r = 0.97$), thus confirming that the four chosen parameters are capable of characterizing to a considerable extent raw meal burnability.

As can be easily observed (Figure 18), the quantity of free lime attributed to the individual parameters varies considerably. Whereas in some mixes the free lime is primarily associated with the chemical parameters (LS/SR), in others the influence of the quartz and calcite grains is predominant.

For example in raw meal no. 3, despite a high overall residue of 24 % on a 90 µm screen, no free lime results from the oversize calcite grains. The reason for this lies in the cement stone composition of this component, in which the individual calcite crystals are fine-grained and homogeneously distributed. The benefit of distinguishing between the overall fineness and the actual dimensions of the individual crystals can thus be appreciated.

In contrast to raw meal no. 3, about half the free lime in raw meal no. 10 is due to oversize calcite, originating from a high-grade limestone component of a titration value of 95 %.

In raw meals no. 46 and 53 the uncombined CaO can be mainly attributed to chemical rather than physical parameters. In the former it is mainly the high silica ratio (3.5), in the latter the very high lime saturation (103 %) which is responsible for the resulting content of free lime. Finer grinding of these raw meals would thus not appreciably lower the

uncombined lime values of clinker burnt in the burnability test. Only a change in chemical composition would improve the burnability of these raw meals.

In raw meal no. 48, despite the large overall residue (43 % > 90 μm) and the given 6.5 % quartz content, the influence of quartz is not unduly great. The reason for this is that the individual crystals are small and well distributed, even within the individual grains.

It is now obvious that by individually examining the 4 parameters which principally influence the burnability, it is easier to characterize, then was previously the case, the critical features of any raw mixture.

It is thus, for instance, easier to decide whether components should be combined or separately ground, or to decide the optimal chemical and physical properties of any raw mix.

5. **THERMOCHEMISTRY OF CLINKER FORMATION**

A detailed discussion of the heat balance of rotary kiln lies outside the scope of this paper and will, in any case, be considered later under the heading of process technology. What will, however, be mainly discussed are the basic thermochemical data relevant of the material aspects of clinker production.

During clinker production, heat is both absorbed (endothermic heat changes) and produced (exothermic heat changes in certain characteristic temperature rings).

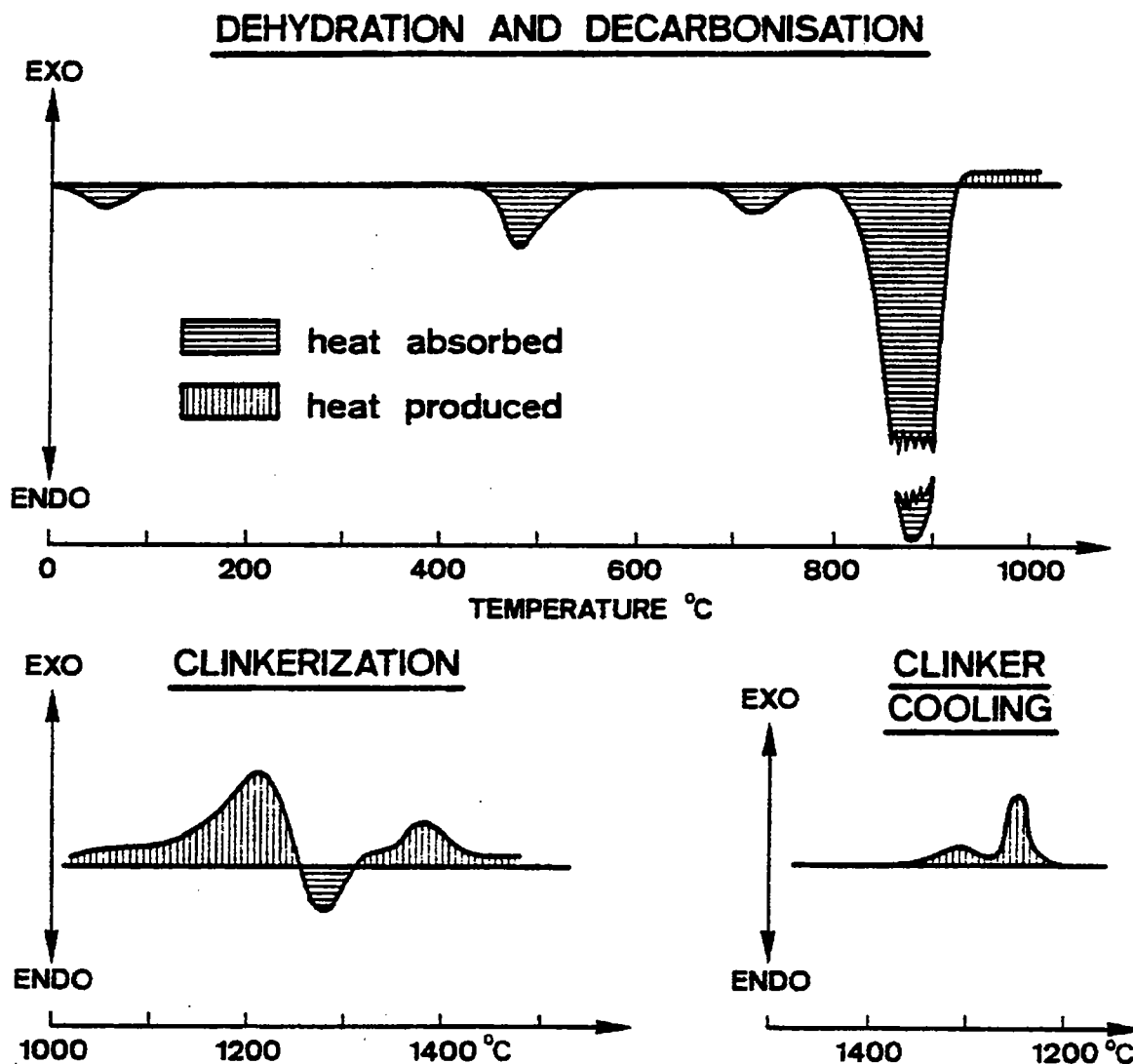
On the basis of the reaction sequence already presented in Table 2, the heat changes pertinent to the individual reactions are known to be as follows:

Table 10 Nature of heat changes occurring during clinkering

Temperature range ($^{\circ}\text{C}$)	Type of Reaction	Heat Change
20 - 100	Evaporation of free H_2O	Endothermic
100 - 300	Loss of physically adsorbed H_2O	Endothermic
400 - 900	Removal of structural H_2O (H_2O , OH groups from clay minerals)	Endothermic
600 - 900	Dissociation of CO_2 from carbonate	Endothermic
> 800	Formation of intermediate products, belite, aluminate and ferrite	Exothermic
> 1250	Formation of liquid phase (aluminate and ferrite melt)	Endothermic
	Formation of alite	Exothermic
1300 - 1240 (cooling cycle)	Crystallization of liquid phase into mainly aluminate and ferrite	Exothermic

A most effective way of visualizing the temperature at which the heat changes occur, their nature and magnitude, can be obtained from differential thermal analysis (DTA) curves of cement raw mixes, an example of which is given in Figure 19.

Figure 19 DTA curves of typical cement raw meals



It is obvious from these curves that by far the greatest heat requirement occurs between 850 - 900 °C, i.e. for the decomposition of the carbonate minerals. The total heat requirements for dehydration, decarbonisation and melting exceed the heat liberated by the formation of belite and the intermediate and final products.

Not included in the DTA representation, however is the heat involved in the actual heating of the raw meal and the cooling of the clinker and of the CO₂ and H₂O gases obtained from the calcite and the clay minerals.

The heat of absorption and liberation, however, varies according to the nature of the individual raw mix, as is clearly demonstrated in Figure 13. **The DTA curve**, therefore, allows a **differentiation of the reactivities** of different raw mixes to be made.

When the **quantitative** values for the various reactions are considered, the heat requirements for the material only with respect to clinker formation may be expressed as follows in approximate terms.

Table 11 Thermal balance of heat changes occurring during clinker formation

Endothermic processes:	dehydration, decreasing, heating	
	kJ/kg clinker	(kcal/kg)
dehydration of clays	≈ 170	≈ 40
decarbonisation of calcite	≈ 1990	≈ 475
heat of melting	≈ 105	≈ 25
heating of raw materials 0 - 1450 °C	≈ 2050	≈ 490
	≈ 4315	≈ 1030
Exothermic processes:	heat of formation, cooling of clinker, CO₂, H₂O	
	kJ/kg clinker	(kcal/kg)
crystallization of dehydrated clay	≈ 40	≈ 10
heat of formation of clinker minerals	≈ 420	≈ 100
crystallization of melt	≈ 105	≈ 25
cooling of clinker	≈ 1400	≈ 335
cooling of CO ₂ (ex calcite)	≈ 500	≈ 120
cooling of H ₂ O (ex clays)	≈ 85	≈ 20
	≈ 2550	≈ 610
Net theoretical heat of clinker formation (endothermic - exothermic)	≈ + 1765	≈ + 420

Depending on the carbonate content, lime saturation and mineralogical composition, the net heat requirement varies between approx. 1630 - 1800 kJ/kg clinker (i.e. 390 - 430 kcal/kg).

These values, of course, only apply to a dry raw meal. For a slurry, the heat requirements will certainly be higher by that necessary of the removal of water. This value will be dependent on the actual slurry water content, and for the average slurry of 35 % H₂O is ≈ 2100 kJ/kg clinker. The **net theoretical heat of formation of 1 kg clinker from slurry is, therefore ≈ 1765 + 2100, i.e. 3865 kJ/kg (920 kcal/kg).**

When considering the heat required for actual clinker production, involving heat losses, the values of approx. 1700 and 3865 kJ/kg clinker are too low. A more realistic heat balance taking process inefficiency into consideration, is approximately as follows:

Table 12 Heat balance of wet and dry kiln

	Dry kiln		Wet kiln	
	kJ/kg clinker			
Evaporation of H ₂ O (0.4 % dry kin and 35 % wet kiln)	≈ 20	(≈ 0.6 %)	2100	(38 %)
Heat of reaction	≈ 1765	(≈ 54 %)	≈ 1765	(≈ 32%)
Heat losses through gas, clinker, dust, etc.	≈ 840	(≈ 26 %)	≈ 1250	(≈ 23 %)
Heat losses by radiation and convection	≈ 650	(≈ 20 %)	≈ 360	(≈ 7 %)
	≈ 3275 kJ/kg		≈ 5475 kJ/kg	

The heat losses due to radiation, exhaust gas, etc. will be explained in more detail under the heading of process technology.

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